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INVESTIGATION OF STRESS CORROSION CRACKING OF TITANIUM ALLOYS

Semi-Annual Progress Report No. 3
for the Period
June 1, 1967 through November 30, 1967

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ABSTRACT

Investigations of the failure of "pure" titanium, Ti-0.2Pd, Ti-6Al-4V, Ti-8Al-1Mo-1V, Ti-5Al-5Sn-5Zr and Ti-6Al-2Sn-4Z4-2Mo alloy foil in methanol solutions have been made. Methanol and water alone without, e.g., halogen ions, will not crack titanium foil.

In addition to chlorides, bromine and sulfuric acid have been added to methanol-water solutions. Bromine causes rapid failure of titanium with up to about 30% water by a corrosion mechanism. Failures in methanol-water-chloride solutions are not considered in all cases to be a stress corrosion cracking mechanism. Acetone behaved similar to water by inhibiting the cracking reaction but DMSO was not an inhibitor. Crack propagation rate measurements varied from 0.15 to 3.90 mm/hr depending upon the alloy and water content of the solution.

Introduction

The progress of the last six months is summarized in this report. The earlier work reported in two previous Semi-Annual Progress Reports was primarily concerned with the cracking of the titanium alloys Ti-6Al-4V (foil and rod), $99^+\%$ Ti (foil) and Ti-13V-11Cr-3Al (foil) in methanol solutions. It was concluded that methanol alone would not cause stress corrosion cracking but that only 0.0001 N NaCl, a few parts per million, would readily cause failure. A small amount of water would prevent cracking, the amount depending primarily upon the quantity and kind of halogen ions present and, secondarily, upon metallurgical variables and surface condition. The mechanism was attributed to electrochemical factors.

Research in the subsequent period has centered on several additional alloys. The effect of organic solvents other than methanol have been investigated. A brief summary of some of the published literature on the cracking of titanium, especially that due to organic liquids, has been completed.

Literature Review

Although titanium and titanium alloys possess excellent mechanical and corrosion resistant properties[1,2,3], as in common with the majority of commercial alloys, they have been found to be susceptible to stress corrosion cracking when exposed to certain environments. The most popular and widely reported environment has

been hot chloride solutions[4,5], although Boyd[6] states that commercially

pure titanium is not susceptible to hot-salt stress corrosion cracking.

More recently failures have been reported in aqueous chloride solutions

at room temperature[7,8,9,18], but in these instances, it is necessary

to use notched specimens, generally precracked by fatigue. In this

respect, the importance of the notch in promoting rupture of the

highly protective oxide film on the metal surface has been convinc-

ingly demonstrated[9]. More recent work[10] indicates that under special

circumstances, preexisting notches are not a prerequisite for crack-

ing in room temperature salt solutions, depending on the surface

preparation the alloy has received. However, it is not necessary to

use precracked specimens to promote cracking in all aqueous environ-

ments at ambient or near-ambient temperatures, as Fontana[11] reported

cracking bent beam specimens of titanium and a Ti-6.8Al - 2.2Sn alloy

in a 10% HCl solution at 35°C. Petersen and Bomberger[12] also observed

cracking of smooth Ti-13V-11Cr-3Al alloy sheets in 5% HCl solution

at room temperature. Cracking of titanium alloys has also been found

to occur in red fuming nitric acid[13] and certain organic liquids, for

example, N_2O_4[14], methanol[15], and saturated hydrocarbons[25].

In the present work, the stress corrosion cracking of smooth

specimens of titanium and titanium alloys is being studied in organic

environments, principally methanol, at room temperature, and, therefore,

the literature pertinent to this environment will now be considered in

greater detail.

Although stress corrosion cracking of smooth specimens can

be produced in methanol environments containing certain "impurities",

a number of investigators have persisted with the usage of precracked
specimens. In such specimens, it might be expected that the phenomenon
of stress corrosion cracking possesses different characteristics and,
therefore, it is difficult to correlate results from the two types of
specimen. However, owing to the shortage of publications relevant
to the present investigation, such results will be considered, although
care must be exercised in their interpretation.

The corrosion resistance of titanium and titanium alloys in
methanol solutions containing bromine has been investigated by
Tomashov[17]. He concluded that corrosion occurred after the bromine
had penetrated the air-formed oxide film and following undermining
of the same. This is not surprising, considering the practical usage
of such solutions in stripping oxide films off steels and titanium
alloys. Also reported was the inhibiting effect of water content and
the tendency to intergranular attack. One of the first reports
concerning the stress corrosion cracking of titanium in methanol
was by some Japanese workers[15] who obtained intergranular cracking
in methanol - 0.4% HCl and methanol - 1% H_2SO_4 solutions. In higher
alcohols and methanol solutions containing more than 1.5% H_2O cracking
was prevented. Prior to both these reports, Meredith and Arter[16]
found that a chlorinated hydrocarbon solution, probably containing
free HCl, was capable of producing cracking in titanium weldments, and
emphasized the importance and necessity of investigating the susceptibility
to stress corrosion carcking of titanium alloy fabrications subjected
to high working stress.

However, not until very recently when the failure of Ti-6Al-4V fuel tanks containing methanol was identified as stress corrosion cracking has the titanium-methanol system been more thoroughly examined. Investigators[19,20] working with material from the failed tanks and also with virgin alloy material of the same composition, in both smooth and precracked specimens, demonstrated the effectiveness of small cathodic currents in stopping cracking and anodic currents in stimulating cracking. The inhibiting effect of water content and an increased susceptibility on aging were also noted. A fractographic examination of the failed specimens revealed features strongly suggesting a mode of cleavage separation to be incorporated in the cracking mechanism. Although reagent grade methanol with no additions was used to promote cracking, work by Haney et al.[21] indicates that methanol itself is insufficient for stress corrosion cracking and "contaminants" in the form of a halide and a minimum water content are also necessary. In the later paper, Meyn[22] using electron fractographic techniques illustrates the differing proportions of cleavage to ductile rupture obtained as a result of the constantly changing stress concentration factor at the crack tip, the higher the latter, the greater the proportion of ductile rupture.

Although Beck[18] has mainly investigated the stress corrosion cracking of precracked specimens of Ti-8Al-1Mo-1V alloys in salt environments, he also reports some work done in methanol in which he obtained stress corrosion cracking[23]. However, on attempting to obtain a correlation between the chloride concentration in the alloy sheet and

the crack velocity, he had no success which is not surprising as
work by Haney et al.[21] clearly demonstrates that it is the halogen
ion in the methanol which produces, at least in part, the susceptibility
to cracking. It must, therefore, be concluded that the methanol Beck
used was contaminated to some degree. Sandoz[24,25] using precracked
specimens of a similar alloy obtained cracking in methanol at approximately
the same stress intensity as in salt water. Although it is apparent
that the importance of "contaminants" in the methanol was not appreciated,
it is worthy of note that he also obtained cracking in longer chain
alcohols and in the hydrocarbons, n-propane, n-heptane, and n-hexane.

Sedriks[26,27] following the work of Tomashov[17], investigated
the stress corrosion cracking of titanium in methanol - 2% Br_2 solution,
by varying the water content. By correlating his results with those
of Tomashov, he found that the maximum susceptibility to cracking
occurred when the grain boundaries were almost passivated, and not
where there was a maximum susceptibility to intergranular corrosion.
Stress is assigned the role of preventing passivation at the crack
tip by causing localized plastic deformation, resulting in rupture
of the protective surface film. In such solutions, there was a critical
water content above which cracking was inhibited, the absolute value
of water content necessary depending on the alloy composition. In
$CH_3OH-HCl-H_2O$ solutions, a sufficient quantity of dimethyl sulfoxide
(DMSO) prevented cracking, and in $DMSO-HCl-H_2O$ solutions no cracking
resulted, which suggested that both CH_3OH and a halogen are required
for cracking to occur. However, recent work by Haney et al. suggests

that DMSO does not inhibit cracking, which can even occur in DMSO-HCl
solutions (see results in present report).

Scully[28], although primarily concerned with the interrelation-
ship existing between hydride formation and stress corrosion cracking
of titanium alloys in salt solutions at elevated and ambient temperatures,
has also observed hydride formation in a Ti-5Al-2.5Sn alloy specimen
after cracking in methanol[6]. Also, work by Haney et al.[21] has shown
that although a small cathodic current is sufficient to prevent
cracking in a Ti-6Al-4V alloy, cracking is reinitiated at higher
current densities. Therefore, although the effects of applied currents
on the stress corrosion cracking of titanium alloys would seem to
be consistent with an active path dissolution mechanism, the available
fractographic evidence indicating embrittlement would seem to suggest
that there is some other factor operating, possibly attributable to
hydrogen or to hydride formation. In this respect, some work by Sedriks[26]
on the failure of a Ti-5Al-2.5Sn alloy in a methanol vapor-air
environment is worthy of mention. Although direct correlations between
the liquid and vapor phases cannot be made, and the results show that
this is indeed the case, nevertheless it is interesting that apparently
it is possible for hydrogen to promote embrittlement in the unstressed
alloy, the process of vacuum annealing being sufficient to remove this
embrittlement. However, such embrittlement is not obtained in liquid
methanol.

The major portion of research into the stress corrosion
cracking of titanium alloys in methanol environments has been instigated

in the last couple of years and most of the details presently reported

represent the state of current research into the problem and must,

therefore, not be regarded as complete. It is probable that continuing

research into the problem will expose many new details which may alter

the interpretation of the results presently obtained.

Materials and Procedures

Investigations of the three alloys mentioned in the introduction

have continued. Several other commercial alloys have been received, namely, two

grades of "pure" titanium, a 0.2% Pd alloy, Ti-8Al-1Mo-1V, Ti-5Al-5Sn-5Zr

and Ti-6Al-2Sn-4Zr-2Mo. The mill compositions of all the alloys investigated

is given in Table I. The tensile properties are presented in Table II.

The titanium with the lowest yield strength and highest purity was obtained

as 0.015" thick sheet which was sheared to quarter-inch wide specimens.

The alloy containing palladium was received as 0.003" thick foil and was

also sheared to quarter-inch wide specimens. All other alloys were

received as foil ($\sim$ 0.003" thick) having been rolled on a Sendzimir mill

and sheared to 1/4" or 1/2" wide strips cut parallel with the rolling

direction by automatic equipment at the mill.

Most of the details of the equipment, apparatus, chemicals and

testing procedures were given in Semi-Annual Progress Report Nos. 1 and 2.

The usual testing procedure for foil was to totally immerse the samples

stressed with a dead weight load equivalent to 85 percent of the yield

strength, unless otherwise noted. Electrode potential measurements were

made on samples with no externally applied stress, and were measured
with the same procedures as described previously. Reported values are
those taken after one hour in solution.

Experimental Results

Methanol-Water-Chloride System

Of particular interest has been the breaking of commercially
pure titanium (75A) as readily as highly alloyed material in methanol
solutions containing small amounts of water and chloride ion. Additional
investigations of a higher-purity commercial titanium alloy (MST-30)
substantiates the previous work on the 75A grade, see Figure 1. Even
with a dead weight load equivalent to only 25 percent of the yield
strength, the specimens broke in about 50 hours in solutions equivalent
to those of the minimum in Figure 1. With no externally applied load,
these fully annealed specimens break apart in the corrosive environment
in a little over a month's time. The ductility and strength drop off
with time as indicated in Figure 2.

Investigations of the effect of the corrosive environment on
cold rolled as well as stress relieved 75A grade foil were made without
an applied load on the specimens. The cold rolled foil was more resis-
tant to deterioration of the tensile properties than the annealed foil
as shown in Table III. The tensile strength and yield strength are
virtually unchanged after a 576 hour exposure, although the percent
elongation has dropped from 8.2 to 3.75 percent. The annealed foil no

longer will support a load equivalent to its original 0.2% off set yield

strength after 240 hours exposure. The elongation has dropped from

26.4 to 2.0 percent. The foils were exposed to solutions approximating

those of their respective maximum susceptibility to cracking as illustrated

in Figure 3.

Investigations of the time to failure and electrode potential

measurements of the latest alloys received reveal only minor differences

either among themselves or with the Ti-6Al-4V or Ti-13V-11Cr-3Al alloys

reported previously, see Figures 4 to 10. Even the commercial alloy

containing palladium shows no especial resistance to failure in the

methanol solutions containing small amounts of water and Cl^- ions,

Figures 9 and 10. The cathodic and anodic polarization of test speci-

ments indicated no significant difference between Ti-0.2 Pd and other

alloys, see Figures 11 and 12.

The effect of impurities that might be found in methanol has

been studied with the $99^+\%$ Ti foil. Additions of acetone, acetic acid

or formaldehyde were made in amounts up to 0.1 percent. In no instance

did the addition significantly change the time to failure or the electrode

potential measurements. Acetic acid showed the greater variation compared

with the results of tests made without such additions, see Figure 13.

Contamination of the methanol with only a few parts per million of

chloride does, however, have a marked effect if no halogen ions are

being added. In testing titanium alloy foil with only methanol-water

solutions and no added chloride, no failures were ever obtained in at

least 500 hours unless contamination by chloride was detected. This would account for the one break reported in the last report for Ti-6Al-4V foil with methanol and 0.05% H_2O.

In the previous progress report, it was noted that acetonitrile-water solutions with 0.01N HCl would not crack Ti-6Al-4V foil. Further work with ethanol and 2-propanol each with water and 0.01N HCl added also will not cause failures. The electrode potential measurements compared with those of acetonitrile and methanol are plotted in Figure 14. No cracking occurred with the addition of NaCl to saturation in either alcohol. However, specimens cracked quite readily with anodic stimulation when immersed in ethanol + 0.01N HCl, see Figure 12. Specimens appeared to break even faster with anodic stimulation than the same alloy in methanol solutions. Breaks were observed for a limited number of specimens in 2-propanol with NaCl with anodic stimulation. However, an apparent film formation made it impossible to maintain a constant current so further investigations were discontinued.

Methanol-Water-Bromine and Methanol-Water-Sulfuric Acid Systems

Others have reported laboratory tests in which bromine or sulfuric acid induced failure of titanium in methanol solutions and our tests add confirmation. Bromine was particularly aggressive to 99^+% Ti foil in either the stress relieved (Figure 15) or the cold rolled condition (Figure 16). With 2% Br_2, the electrode potential values were difficult to reproduce because the specimen corroded excessively with less than about 10 percent water. Thus, the values were not plotted.

With no applied stress, it would be expected that deterioration of the titanium would be rapid to exposure of only 0.1% Br_2 in methanol. Such tests were made for solutions with water contents up to 30 percent and the results are presented in Table IV. After only one hour exposure to the one percent water solution, the tensile strength dropped to below that of the original 0.2% off set yield strength of the cold rolled 99^+% Ti foil. However, with added water, any given time of exposure showed less deterioration of the foil. Again, the cold rolled foil appeared to be more resistant than the stress-relieved foil.

The addition of one percent H_2SO_4 (0.36N) to methanol-water solutions produced failures with the Ti-6Al-4V alloy, Figure 17. Reducing the H_2SO_4 content to 0.02N made very little change in the time to failure values but the minimum in the curve did shift toward higher water contents in contrast with chloride containing methanol solutions. Up to the present time, it has not been possible to break Ti-8Al-1Mo-1V foil in H_2SO_4 containing solutions.

Electrode Potential Measurements

Electrode potential measurements have been found to be a valuable aid in determining what solutions would be the most aggressive to a given titanium alloy. For methanol solutions containing halogen ions, it was found that the minimum in the time to failure curves always occurred in solutions which gave a one-hour electrode potential reading of between -40 and -200 mv. (S.C.E.), e.g., see Figures 1, 3 to 10 and 19 to 23 in this report. It was evident that when molecular bromine

or H_2SO_4 was added to methanol, the correspondence no longer applied, e.g., see Figures 15, 16 and 17.

In view of the correspondence for methanol containing halogen ions, it is not surprising that ethanol-water, 2-propanol-water and acetonitrile-water would not crack the titanium. The electrode potential values for all three systems were very positive, see Figure 14. On the other hand, electrode potential values in the range -40 to -200 mv. (S.C.E.) do not necessarily mean the titanium will fail. To illustrate the point, observe Figure 18 which shows the effect of HCl and tetramethyl-ammonium chloride on the electrode potential measurements in the acetonitrile-water system. Note that in water the electrode potential values were comparable, yet at high concentrations of acetonitrile there was a spread of over 500 mv. dropping the values for the solutions with tetramethylammonium chloride into the range where cracking of titanium might be expected. However, no failures were observed within 500 hours with a few specimens stressed to 85% Y.S. Tetramethylammonium chloride is dissociated to a much greater degree than is HCl in acetonitrile, and this would presumably account for the difference in the electrode potential measurements.

Methanol with Dimethylsulfoxide or Acetone and Chlorides

Investigations of the effectiveness of solvents other than water to inhibit the cracking of titanium in methanol have been under study. Dimethylsulfoxide (DMSO) and dimethylketone (acetone) have similar

structures except for the respective sulfur or carbon atoms and each is completely miscible in methanol. The two solvents have some properties which are similar to those of water due perhaps to the partial negative charge on the oxygen atom.

Methanol and water solutions with 0.01N HCl produce a maximum susceptibility to stress corrosion cracking at 0.6% water for the cold rolled 99^+%Ti foil, Figure 19. With acetone, the minimum in the time to failure curve occurred at about 1.3% $(CH_3)_2CO$, Figure 20, making acetone not as effective as water as an inhibitor. DMSO had almost no inhibiting effect, see Figures 21 and 22. The maximum susceptibility to cracking occurred at about 90% $(CH_3)_2SO$ whether NaCl or HCl was added. The major difference seems to be that 0.01N HCl added to pure DMSO readily cracked the titanium loaded to 85% Y.S., but 0.01N NaCl did not. When 0.4% water was added to the methanol-DMSO-0.01N NaCl system, the cracking was inhibited but not uniformly as shown in Figure 23.

Crack Propagation Rates

Since the last report, work has been continued on the measurement of crack propagation rates on foil specimens of titanium and titanium alloys, in methanol. Variables such as solution composition and applied stress have been introduced into the system. In the previous work, the specimens had been tested at solution compositions where there is a maximum susceptibility to stress corrosion cracking, i.e., at compositions corresponding to the minimum in the time to failure curve for the particular material, and at 75% yield strength. The experimental procedure for the determination of crack propagation rates was the same as that used previously.[21]

The table below shows the results obtained from such tests, together with the particular solution compositions used. The 99^+%Ti was used as cold rolled and stress relieved, the Ti-0.2Pd and Ti-8Al-1Mo-1V as cold rolled, the Ti-5Al-5Zr-5Sn as partially annealed and the Ti-6Al-4V as cold rolled and annealed.

Crack Propagation Studies of Titanium and Titanium Alloys in Methanol Solutions

Alloy	Curve No.	% H_2O	Halogen Ion Source	% Y.S.	Incubation Time, Hr.	Propagation Time, Hr.	Propagation Rate, mm/hr.
99^+%Ti	①	0.65	0.01N NaCl	75	2.75	0.50	3.50
99^+%Ti	②	0.55	0.01N HCl	75	1.75	1.00	1.00
99^+%Ti	③	0.02	0.01N NaCl	75	20.00	14.00	0.15
99^+%Ti	④	0.50	0.01N NaCl	60	3.80	1.20	1.50
Ti-0.2Pd	⑤	0.25	0.01N NaCl	75	2.25	2.00	~0.40
Ti-6Al-4V	⑥	0.30	0.01N NaCl	75	0.75	0.50	3.30
Ti-5Al-5Zr-5Sn	⑦	0.10	0.01N NaCl	75	0.62	0.43	2.20
Ti-8Al-1Mo-1V	⑧	0.50	0.01N NaCl	75	0.75	0.25	3.90

Figure 24 shows the corresponding data used to obtain the crack propagation rates, plotting maximum crack depth as a function of time exposed to the solution. The numbered curves refer to the alloys and testing conditions as indicated in the above table.

Although from the results, per se, no definite conclusions can
be made, they do, however, exhibit a number of interesting trends which
indicate the importance of both electrochemical and deformation effects,
and also possible directions in which further investigation may be
directed.

In the 99^+%Ti, reduction in applied stress or in water con-
tent produce similar effects in that the incubation and propagation
times are increased, resulting in slower crack propagation rates. The
longer incubation time at the lower stress level is probably simply
reflecting the necessity for a critical stress intensity to be attained,
whereas the effect of lower water content demonstrates the importance
of solution composition for crack initiation. Also shown is the depen-
dence of crack propagation on the deformation and solution composition
at the crack tip. Although substitution of 0.01N HCl for 0.01N NaCl
similarly increases the propagation time resulting in a slower crack
propagation rate, there are important differences, in that the incubation
time, in fact, decreased resulting in a shorter time to failure. This
example serves to illustrate the general point that it is important to
distinguish between the incubation and propagation times in relationship
to total failure times. If the crack propagation rate is considered a
measure of the susceptibility to stress corrosion, then in this instance
the specimen is more susceptible in the solution containing 0.01N NaCl
although longer failure times are produced. It is possible that the
shorter incubation time is related to corrosion effects in that titanium

possesses excellent corrosion resistance in most neutral salt solutions

but is readily corroded in certain acid solutions, e.g., HCl. This

might then serve to explain the slower propagation rate, as increased

corrosion at the crack tip would result in blunting of the same and

a consequent lowering of the stress intensity. This receives additional

support from the reduction in propagation rate which occurs when the

applied stress is decreased. (Figure 24, curves ① and ④ .)

Figure 24 illustates very effectively the similar stress

corrosion properties with respect to cracking characteristics, existing

between the alloys Ti-6Al-4V, Ti-8Al-1Mo-1V and Ti-5Al-5Zr-5Sn (curves

⑥ , ⑦ , and ⑧); and comparing these curves with that for 99+%Ti under

similar conditions of testing (curve ①), it can be seen that the main

difference lies in the longer incubation period. However, the curve

for the Ti-0.2Pd alloy, although showing an incubation time close to

that for titanium also shows a vastly reduced crack propagation rate

(curve ⑤). These results may be interpreted in terms of the differing

surface film and corrosion properties of the alloys. It can be postulated

that the longer incubation times in 99+%Ti and the Ti-0.2Pd alloy are

due to different surface film characteristics, resulting perhaps from

surface compositional differences, whereas the similar propagation rates

existing between 99+%Ti and the alloys, excepting Ti-0.2Pd, perhaps

indicates some common factor operating in the cracking mechanism. If

the mechanism of cracking is largely attributed to electrochemical factors,

as indeed was suggested by a previous report[21], then the slower propaga-

tion rate in the Ti-0.2Pd alloy almost certainly reflects its superior

corrosion resistance.

Discussion

The experimental results obtained with methanol solutions
since the last semi-annual report would not indicate any changes in
the suggested mechanism of stress corrosion cracking. The cracking
mechanism is predominantly electrochemical in character, with
metallurgical factors being of secondary importance. The cracking
can be inhibited with small additions of water probably by passivation.
The maximum susceptibility occurs in solutions which do not quite
inhibit the cracking reaction. The experimental evidence continues
to indicate that titanium failures do not occur in methanol solutions
without a few parts per million of Cl^-, Br^- or I^- ion. Small amounts
of sulfuric acid added to methanol could be included at least for the
Ti-6Al-4V alloy but not all titanium alloys appear to be susceptible.
Bromine also might be included as one of the possible aggressive agents
except that it is doubtful that the mechanism of failure is stress
corrosion cracking.

The corrosion of titanium in methanol solutions containing
bromine has been investigated by Tomashov et al.[17] They found that
the general corrosion rate could be lowered substantially by water
additions, but that the tendency to intergranular corrosion goes
through a maximum at intermediate water contents before decreasing
uniformly. Sedriks et al.[26] combined their results on the susceptibility

of titanium to stress corrosion cracking in a methanol solution containing

2% Br_2 with those of Tomashov, and found that the maximum susceptibility

to stress corrosion cracking occurred at a higher water content than

the maximum susceptibility to intergranular corrosion. They concluded

that such results indicated that the mechanism was not simply stress-

aided intergranular corrosion. However, West[29] suggests that the

purported stress corrosion cracking in reality consists solely of the

mechanical parting of corroded material, with the stress producing no

detectable increase in the rate of grain boundary penetration.

In the present work, the experimental results (see Table IV)

certainly appear to lend support to the latter viewpoint. Under stresses

of 75% yield stress and below water contents of 25%, times to failure

were between one and two hours, and in comparable times it can be seen

that the elongation has been reduced by 50% and by as much as 75% in

the lower water content solutions, after exposure to the solutions

without applied stress. In the annealed titanium where the failure

times are shorter, the enhanced susceptibility to corrosion is illustrated

in the value of the elongation which shows a deterioration of approximately

95% after one hour exposure to a solution containing 1% water, without

applied stress. The increased reactivity is also illustrated in the

more active surface potential measurements. Conversely, in a solution

containing 30% H_2O very little change in the tensile properties resulted

after 24 hours exposure in the unstressed state, and no failure was

recorded up to 500 hours exposure when stressed to 75% yield stress.

These results are considered to be in agreement with a mode of failure

involving purely corrosive action, rather than stress corrosion cracking.

The deterioration of the tensile properties of annealed

titanium without an applied load in methanol-water-choride solutions

also suggests that the mechanism might not be strictly stress corrosion

cracking. Cold rolled 99+%Ti foil shows virtually no loss in tensile

and yield strengths after more than 500 hours exposure even though

the measured elongation dropped. After annealing, the foil exhibits

a marked decline in tensile and yield strengths as well as the percent

elongation within less than 200 hours exposure (Table III). Similar

observations were made for the higher purity titanium fully annealed,

Figure 2, suggesting that when some degres of recrystallization has

occurred the predominant mechanism appears to be intergranular corrosion

or stress accelerated corrosion.

Crack propagation rates for the stress relieved 99+%Ti foil

ranged from 3.50 to 0.15 mm/hr depending in particular upon the amount

of water in the methanol, see table, page 15. The faster rates occurred

in the range of water contents where the shortest times to failure

were observed. Rates of about 4 mm/hr have been found by the workers

for certain systems involving stress corrosion cracking,[30] thus suggesting

that perhaps more than one mechanism may be involved for the cracking

of titanium depending upon the water content in the methanol.

The effect of acetone in inhibiting the cracking caused by

methanol and halogen ions makes it evident that water is not the only

inhibitor. The addition of other organic liquids to methanol is currently under study both to determine which ones will inhibit the reaction as well as to attempt to understand the mechanism of cracking by methanol. Thus additional discussion should await the next report.

Conclusions

The following conclusions are based on the work accomplished in the period June through November, 1967.

1. Titanium foil, whether alpha, alpha + beta or beta alloy, was susceptible to failure in methanol with small amounts of water and 0.01N NaCl or HCl when stressed to 75% of yield strength. Although 0.02 N H_2SO_4 added to methanol with small amounts of water will crack Ti-6Al-4V foil, the 8Al-1Mo-1V foil does not seem to be susceptible.

2. Bromine added to methanol-water solutions caused failures of 99^+%Ti foil by a mechanism involving corrosive action alone with up to about 30% water. The action appears to be inhibited by additions of 30% water. Methanol-water solutions containing the chloride ion appeared to cause stress corrosion cracking if the 99^+%Ti foil was cold rolled, but not if the foil was annealed, in which case there was some evidence to suggest intergranular corrosion or stress accelerated corrosion.

3. Impurities added to methanol-water-choride solutions only make minor changes in the cracking tendencies of 99^+%Ti foil, namely, 0.1 percent acetone, formaldehyde, or acetic acid.

4. No cracking of titanium alloys was observed with ethanol-water-chloride or 2-propanol-water-choride solutions in 500 hours without anodic stimulation. Electrode potential measurements confirmed that cracking would not be expected.

5. Acetone, as well as water, will inhibit the cracking of titanium in methanol-chloride solutions but DMSO will not.

Future Work

The following work has been planned for the immediate future.

1. Correlation between forms and magnitudes of electrode potential measurements, particularly with respect to effects of organic additions to the methanol, and stress corrosion characteristics.

2. Further investigation of crack propagation rates with respect to metallurgical and chemical variables.

3. Examination of stress corrosion cracking in methanol-sulfuric acid containing solutions where it would appear that metallurgical variables, e.g. alloy composition, have an important effect.

4. Additional work with specimens machined from rod is planned for a hard-beam tensile machine.

5. Thin film work to determine initiation sites for stress corrosion cracking.

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TABLE I

Chemical Composition, Weight Percent

Alloy	Designation	Al	V	Mo	Zr	Sn	Cr	Pd	Fe	O_2	C	N_2	H_2
99.5 Ti (sheet)	MST-30												
99.0 Ti (foil)[†]	Ti-75A								.14	.38(max.)	.025	.016	.005
Ti-Pd (foil)	Ti-0.20 Pd							.20					
6Al-4V (foil)	Ti-6Al-4V	6.0	4.0						.21	.134	.02	.01	.001
6Al-4V (rod)	MST-6Al-4V	6.3	4.2						.24	.102	.02	.007	.006
5Al-5Sn-5Zr (foil)	Ti-5Al-5Sn-5Zr	5*			5*	5*							
8Al-1Mo-1V (foil)	Ti-8Al-1Mo-1V	7.9	1.0	1.1					.05	.09	.025	.012	.009
6Al-2Sn-4Zr-2Mo (foil)	Ti-6Al-2Sn-4Zr-2Mo	6*		2*	4*	2*							
13V-11Cr-3Al (foil)	Ti-13V-11Cr-3Al	3*	13*				11*		.08	---	.016	.017	.007

* Nominal

† First lot

TABLE II

Mechanical Properties of Titanium Alloys

Alloy	Treatment	Tensile Strength, KSI	Yield Strength, KSI 0.2% off set	Elongation, % in 4 in.
99.5 Ti (sheet)	Cold rolled	119.3	98.5	6.2
99.5 Ti (sheet)	Annealed 2 hr. at 1300°F	50.6	31.7	31.0
99.0 Ti (foil)†	Cold rolled	137.8	124.5	6.2
99.0 Ti (foil)†	Annealed 2 hr. at 1025°F	90.0	80.8	21.5
99.0 Ti (foil)†	Annealed 2 hr. at 1300°F	100.4	81.6	28.0
99.0 Ti (foil)*	Cold rolled	142.2	129.3	7.2
99.0 Ti (foil)*	Annealed 2 hr. at 1025°F	90.8	74.5	29.9
Ti-0.20 Pd (foil)		72.9	58.8	23.0
Ti-6Al-4V (rod)	Hot rolled and annealed	144.0	143.5	8.2 (in 1.25 in.)
Ti-6Al-4V (foil)	Cold rolled and annealed	170.5	131.7	12.8
Ti-5Al-5Sn-5Zr (foil)	Cold rolled and partially annealed	156.4	138.7	3.9
Ti-8Al-1Mo-1V (foil)	Cold rolled	114.7	104.6	3.8
Ti-6Al-2Sn-4Zr-2Mo(foil)	Cold rolled	190.4	147.3	5.1
Ti-13V-11Cr-3Al (foil)	Cold rolled	181.6	172.8	3.75
Ti-13V-11Cr-3Al (foil)	Slow heat to 1400°F, held 10 min. and C.W.Q. + 24 hr. at 900°F	175.2	165.6	4.88

† First lot

* Second lot (S206)

TABLE III

Tensile Properties of 99+% Ti* Foil After Exposure to Indicated Corrodant with No Applied Load

Cold Rolled Foil Exposed to CH₃OH + 0.01N NaCl + 0.2% H₂O

Time in Solution, Hr.	% Elongation	Tensile Strength, KSI	Yield Strength, KSI, 0.2% off set
0	8.2	139.7	132.9
8	5.7	140.3	134.2
24	4.8	140.3	132.9
104	4.1	139.1	131.7
144	4.7	142.8	134.2
192	3.5	140.3	132.9
240	4.0	142.8	131.7
576	3.8	137.8	132.9

Foil, Cold Rolled and Annealed 2 hrs. at 1025°F, Exposed to CH₃OH + 0.01N NaCl + 0.5% H₂O

Time in Solution, Hr.	% Elongation	Tensile Strength, KSI	Yield Strength, KSI, 0.2% off set
0	26.4	87.4	71.4
6	7.5	77.5	67.7
24	3.5	74.5	71.4
144	3.0	70.8	68.9
240	2.0	67.7	--
408	2.0	66.5	--
960	1.4	54.2	--

*Second lot (S206)

TABLE IV

Tensile Properties of 99+%Ti* Foil After Exposure to
Indicated Corrodant with No Applied Load

Cold Rolled Foil Exposed to CH_3OH + 0.1% Br_2 + 1.0% H_2O

Time in Solution, Hr.	% Elongation	Tensile Strength, KSI	Yield Strength, KSI, 0.2% off set
0	8.2	139.7	132.9
0.5	3.2	134.2	129.2
1	2.1	123.2	---
6	0.8	46.8	---
16	0	---	---
24	0	---	---

Cold Rolled Foil Exposed to CH_3OH + 0.1% Br_2 + 12.0% H_2O

0	8.2	139.7	132.9
0.5	3.8	141.5	135.4
1	2.7	137.8	134.2

Cold Rolled Foil Exposed to CH_3OH + 0.1% Br_2 + 16.0% H_2O

0	8.2	139.7	132.9
0.5	5.4	142.8	137.8
1	3.6	137.8	132.9
6	2.1	128.0	---
16	2.1	130.5	---
24	2.6	135.4	131.7

(continued)

TABLE IV (continued)

Tensile Properties of 99+%Ti Foil After Exposure to Indicated Corrodant with No Applied Load

Cold Rolled Foil Exposed to $CH_3OH + 0.1\% \ Br_2 + 30.0\% \ H_2O$

Time in Solution, Hr.	% Elongation	Tensile Strength, KSI	Yield Strength, KSI, 0.2% off set
0	8.2	139.7	132.9
24	7.8	139.1	132.9

Foil, Cold Rolled and Annealed 2 hrs. at 1025°F, Exposed to $CH_3OH + 0.1\% \ Br_2 + 1.0\% \ H_2O$

0	29.9	90.8	74.5
1	1.2	55.4	---

* Second lot (S206)
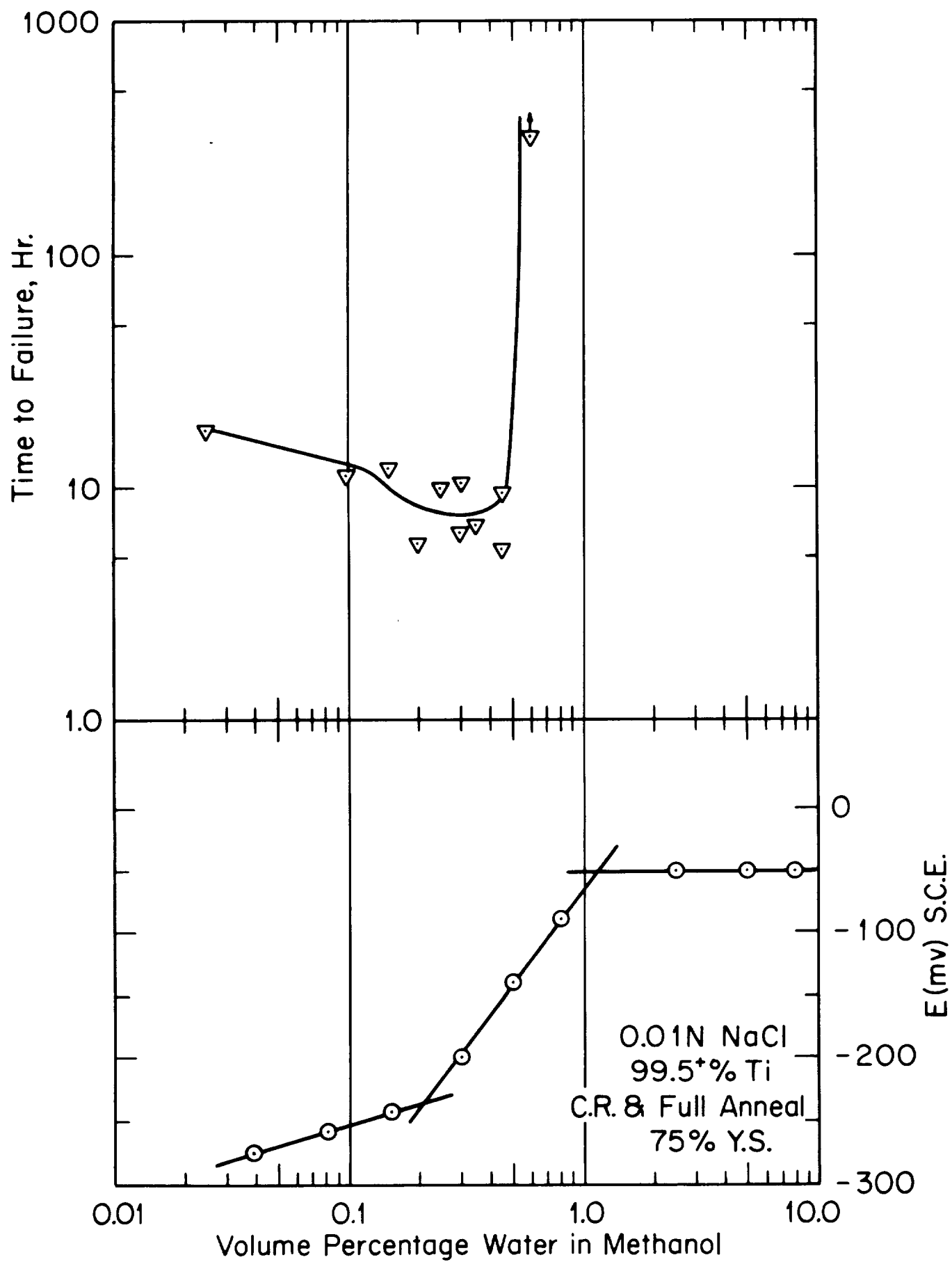
Figure 1   Comparison of time to failure with one-hour electrode potential value.
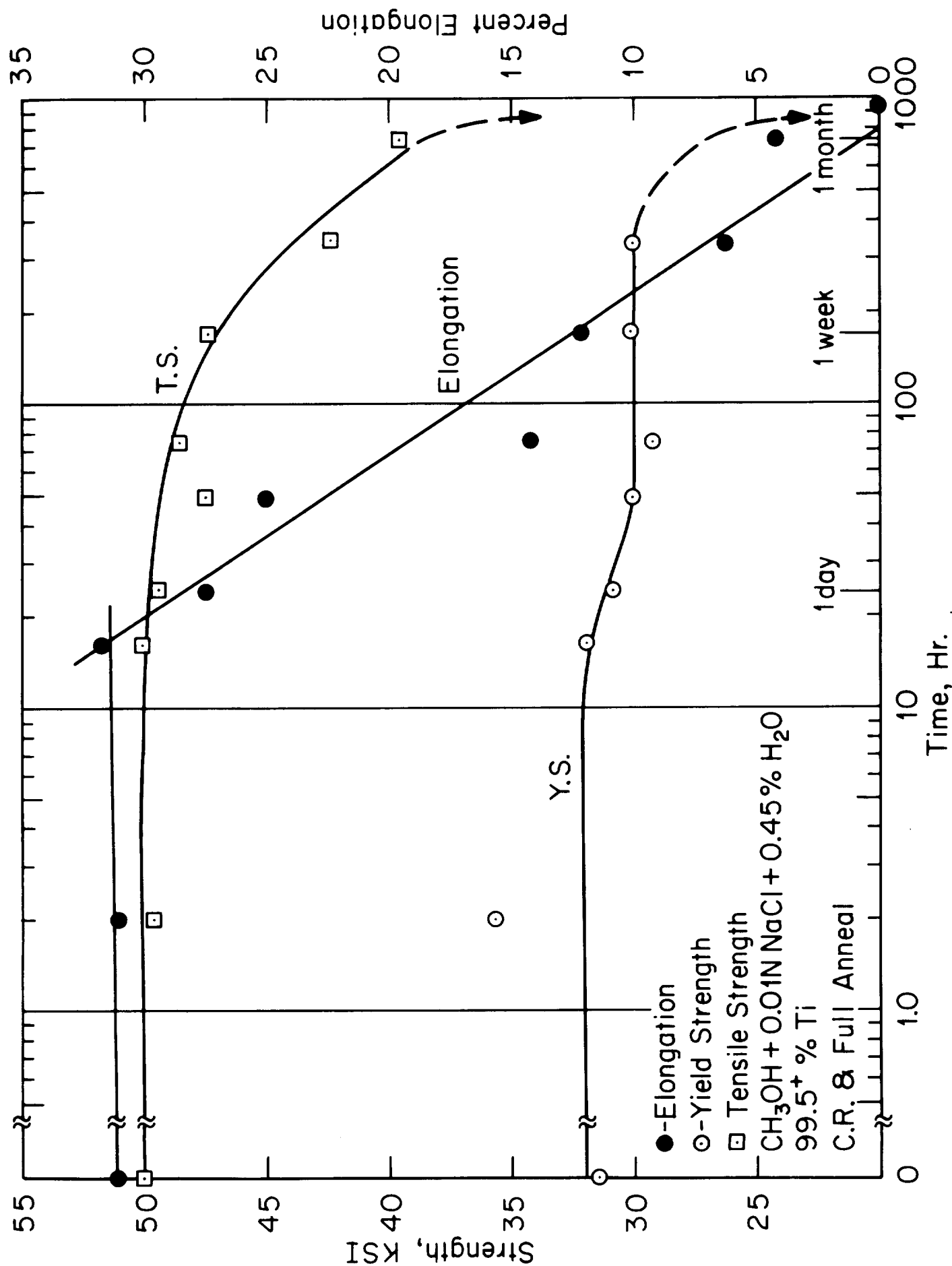
Figure 2 Tensile properties of 99.5+%Ti sheet after exposure to methanol solution containing 0.01N NaCl and 0.45% H₂O with no applied load.
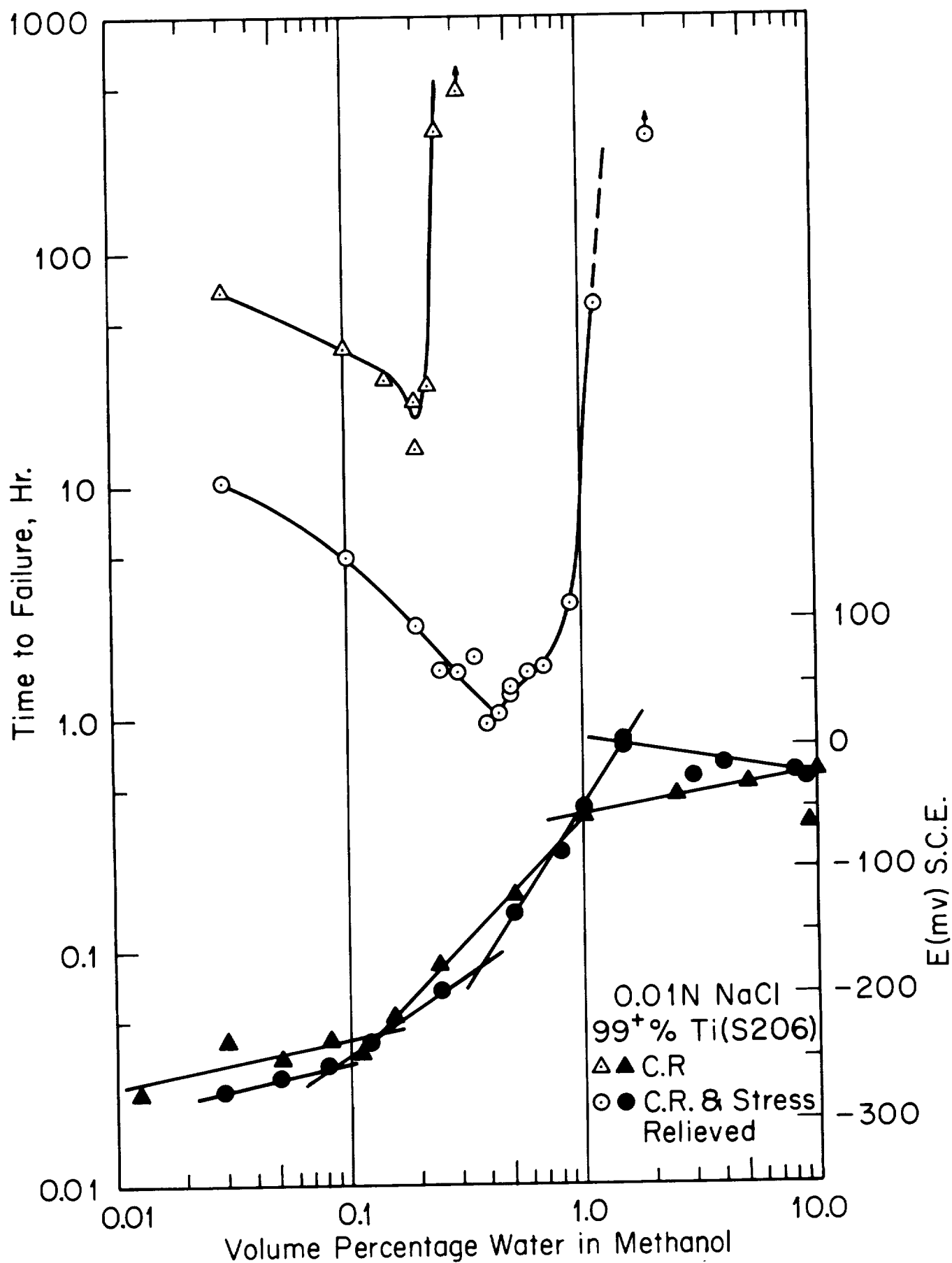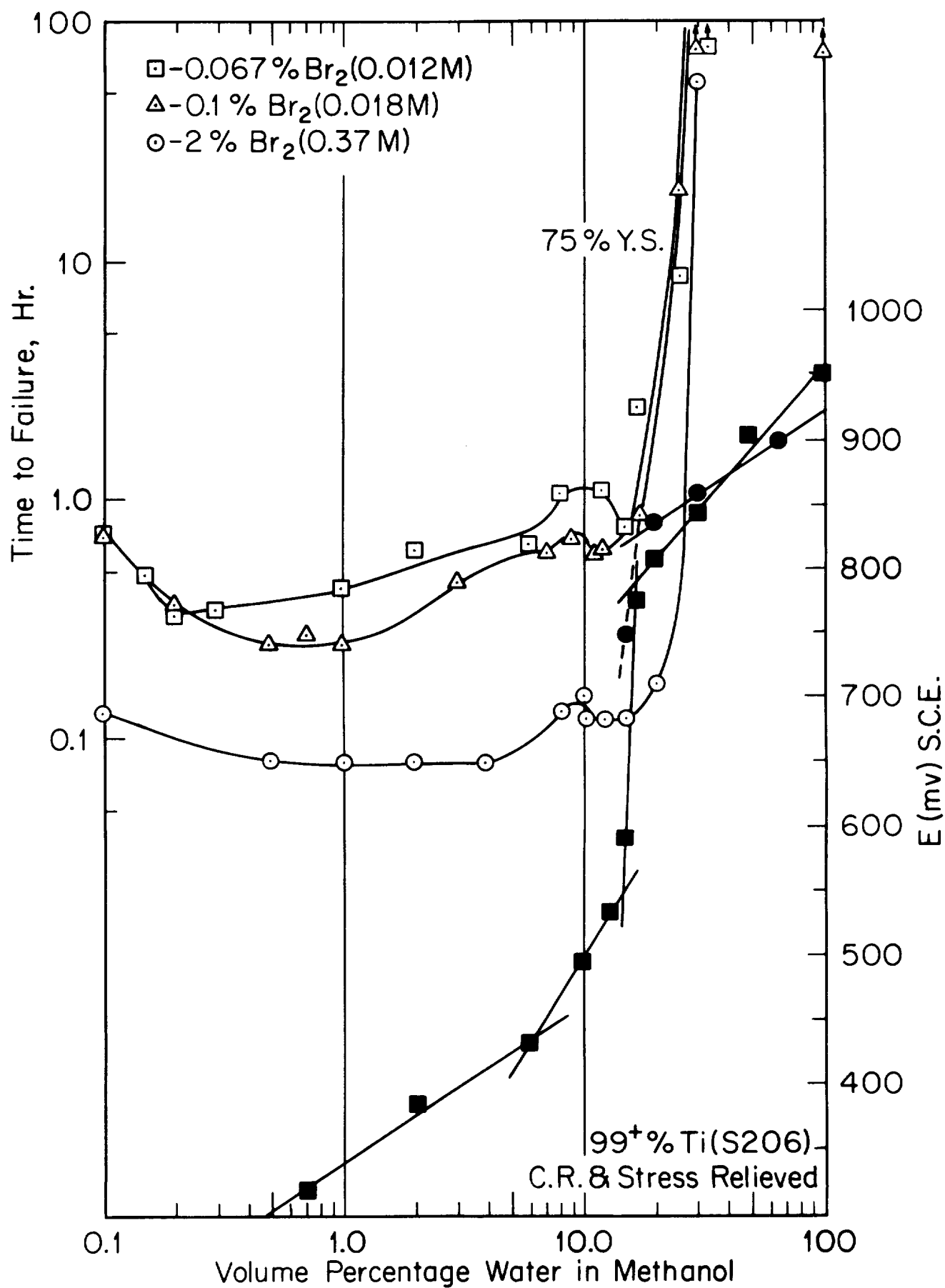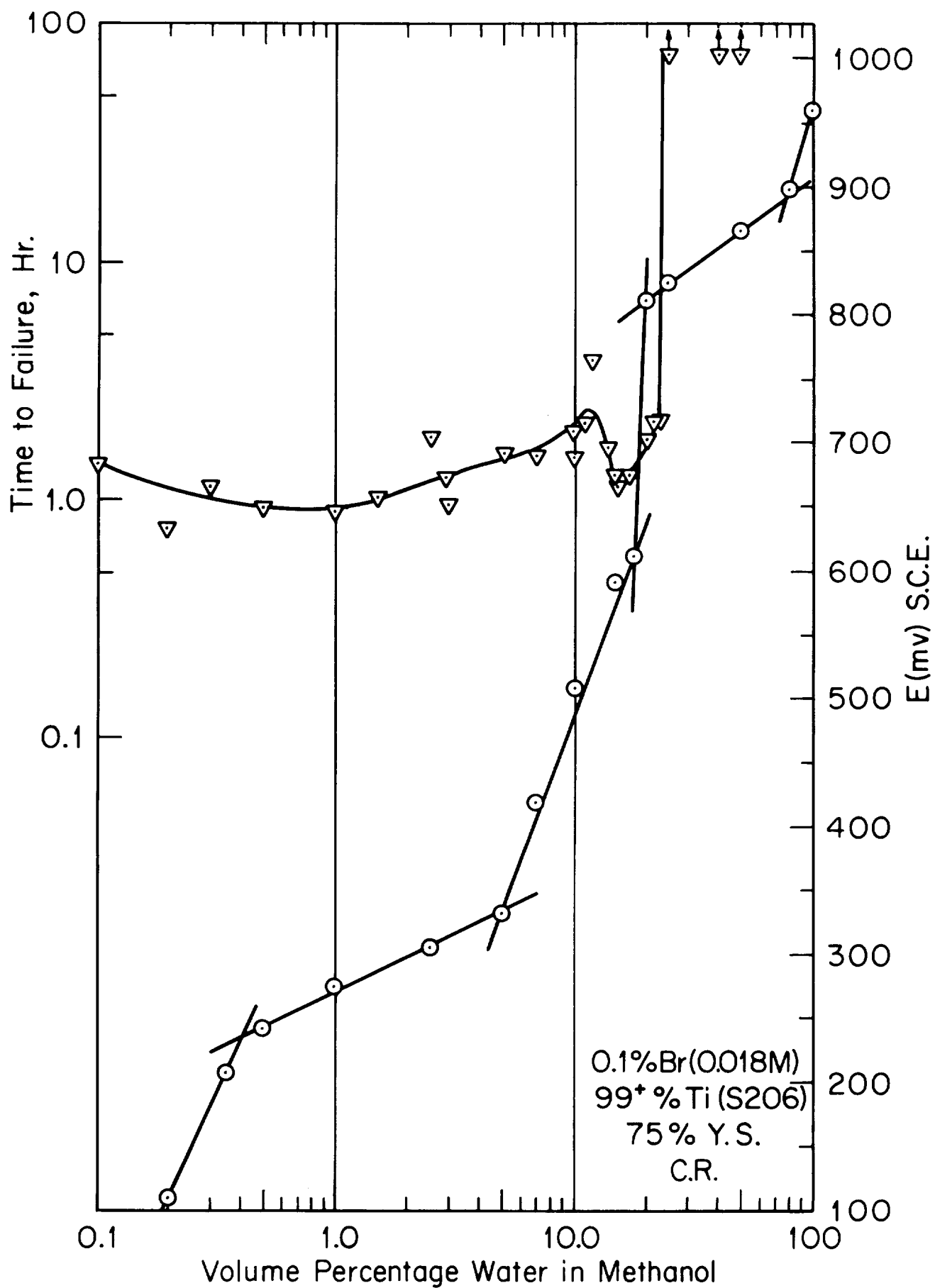
Figure 3   Effect of cold rolling and stress relief anneal on time to failure and one-hour electrode potential value.
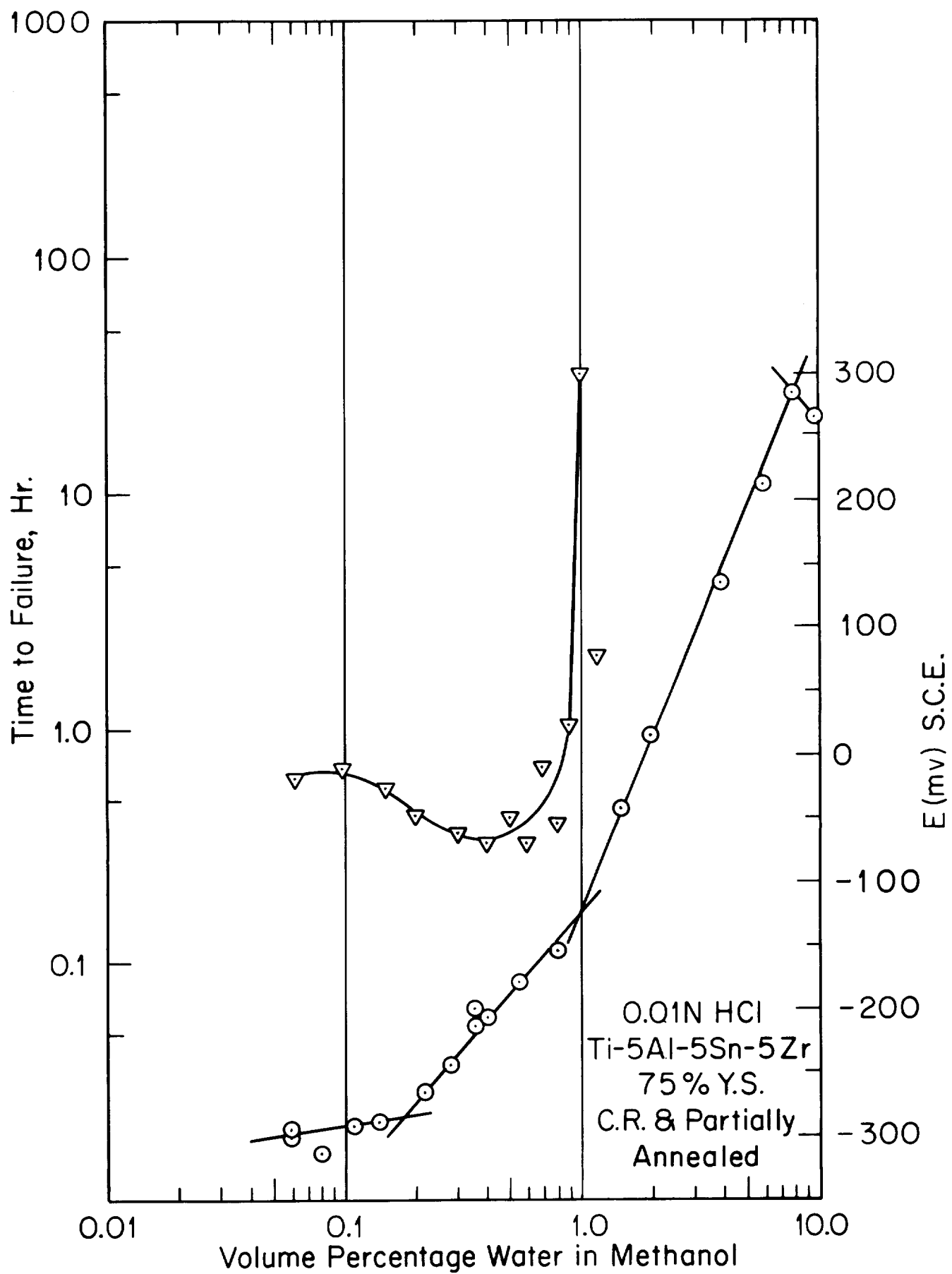
Figure 4   Comparison of time to failure with one-hour electrode potential value.
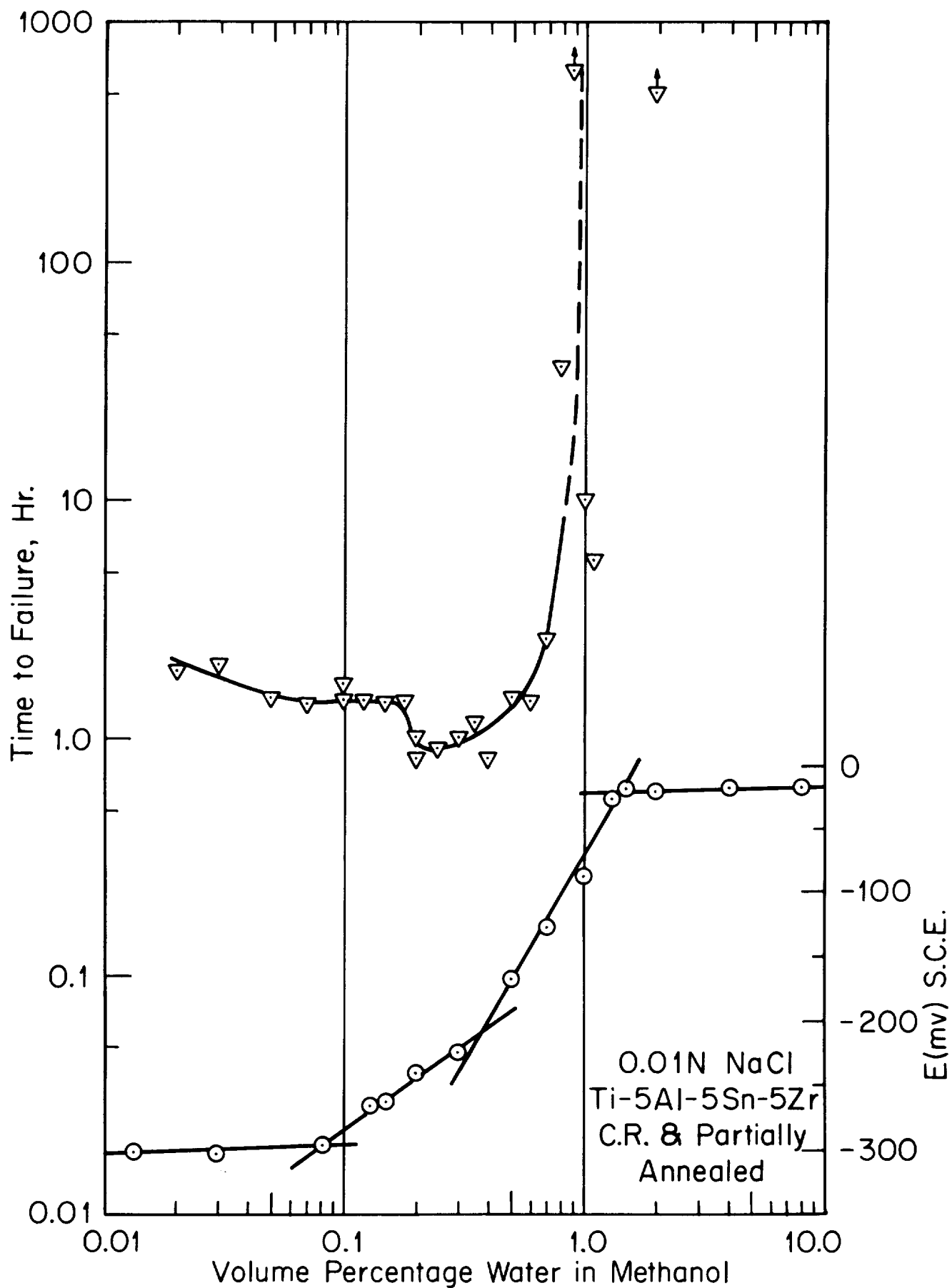
Figure 5 Comparison of time to failure with one-hour electrode potential value.
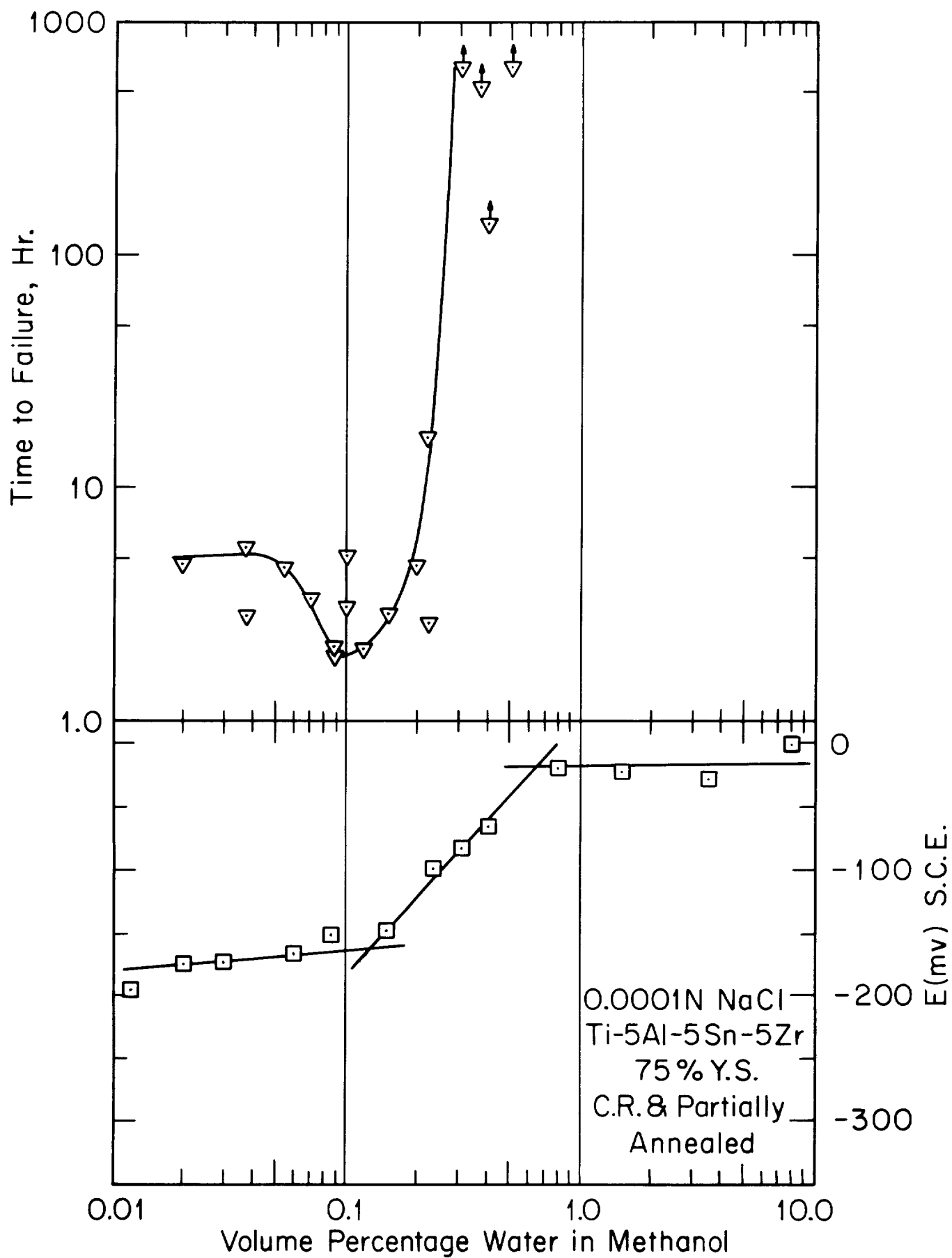
Figure 6 Comparison of time to failure with one-hour electrode potential value.
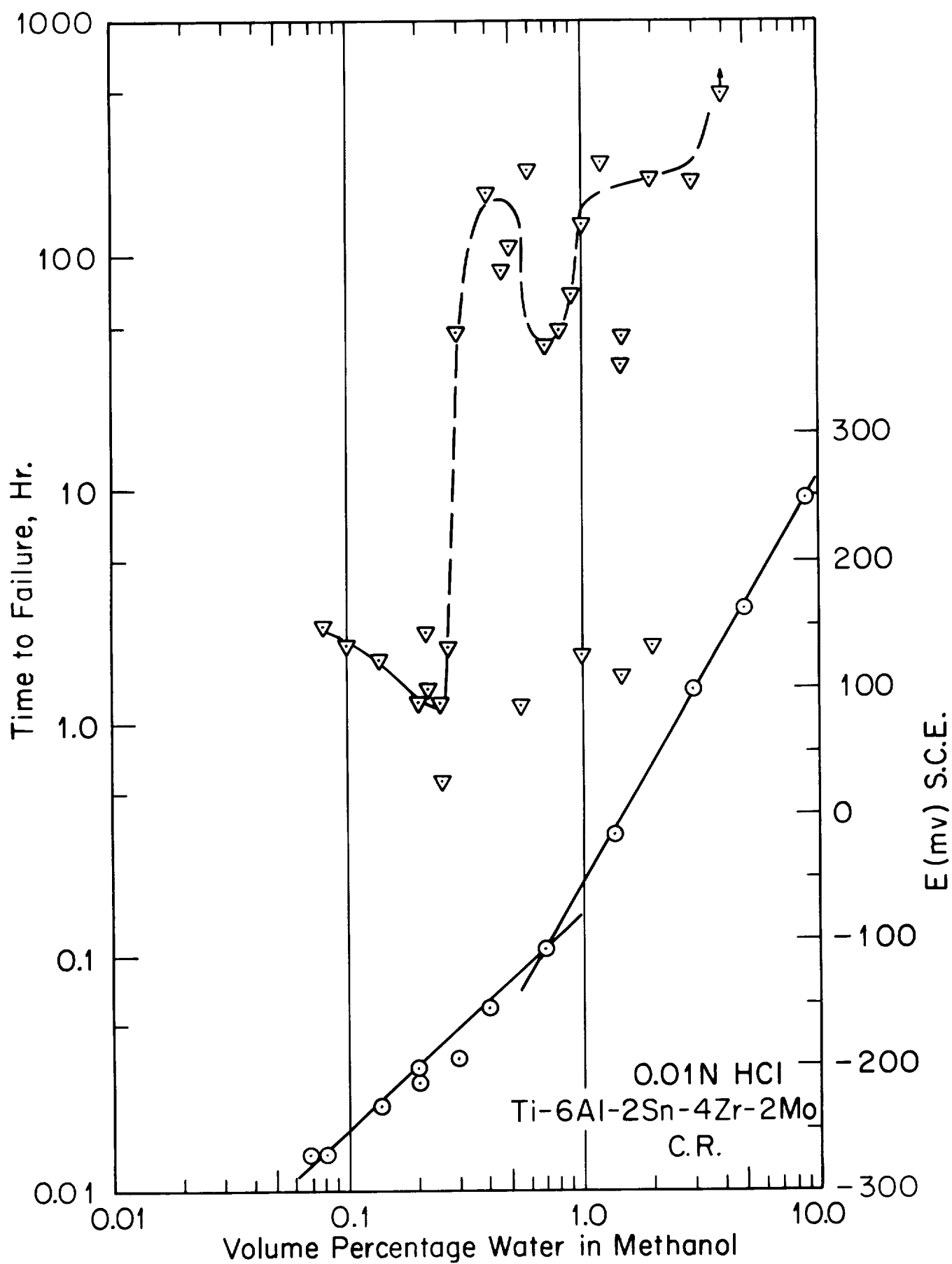
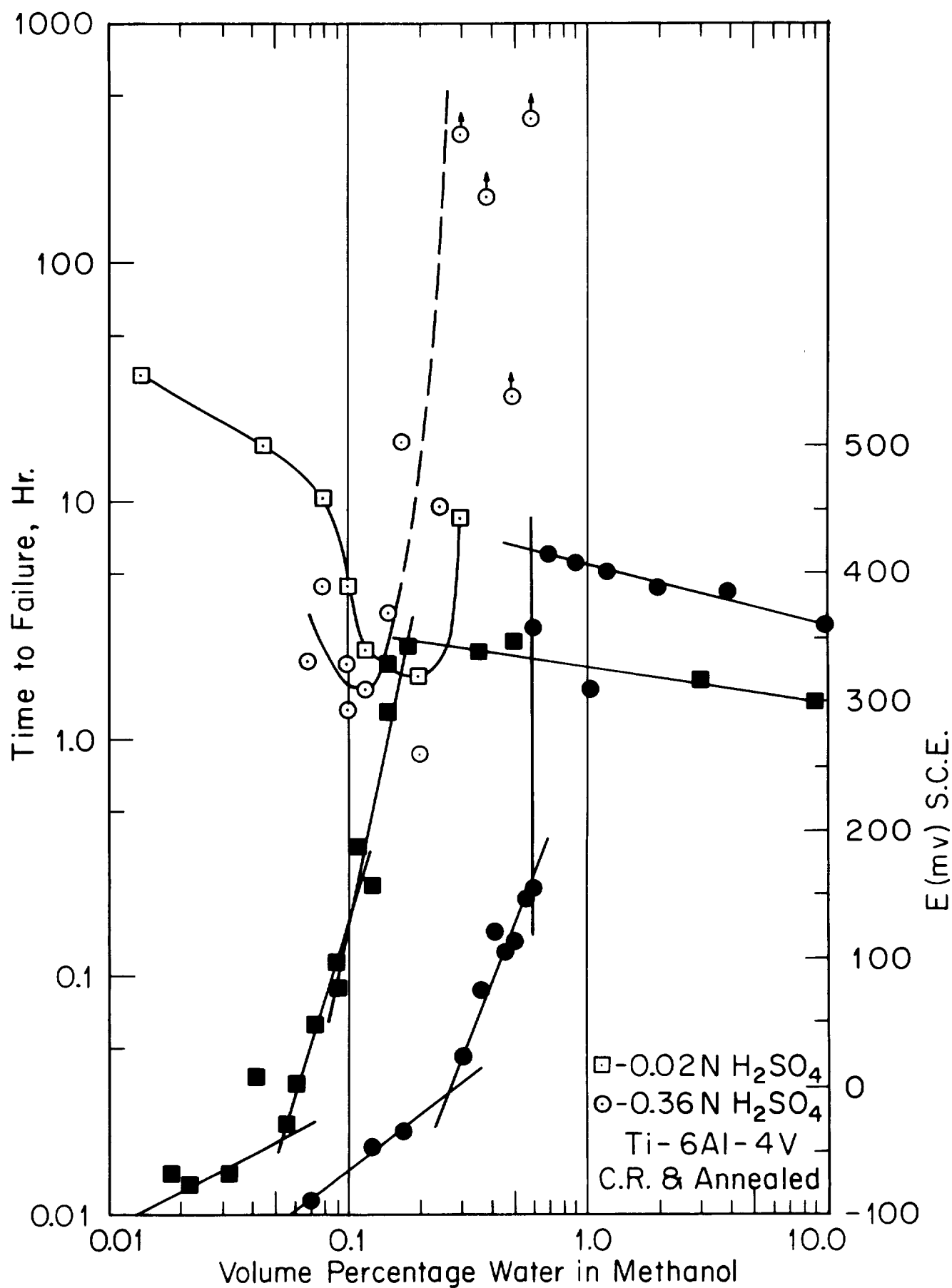Figure 7 Comparison of time to failure with one-hour electrode potential value.
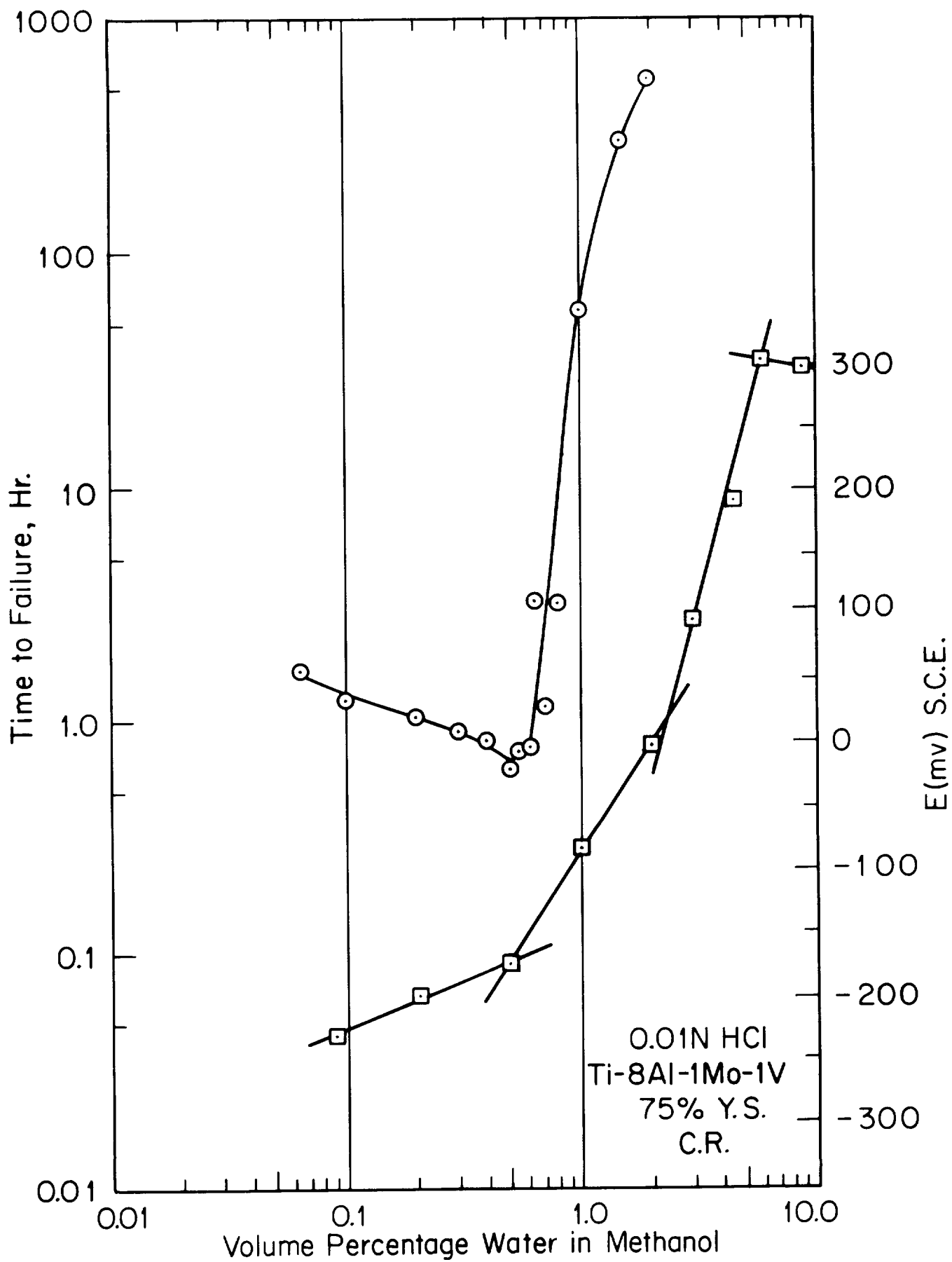
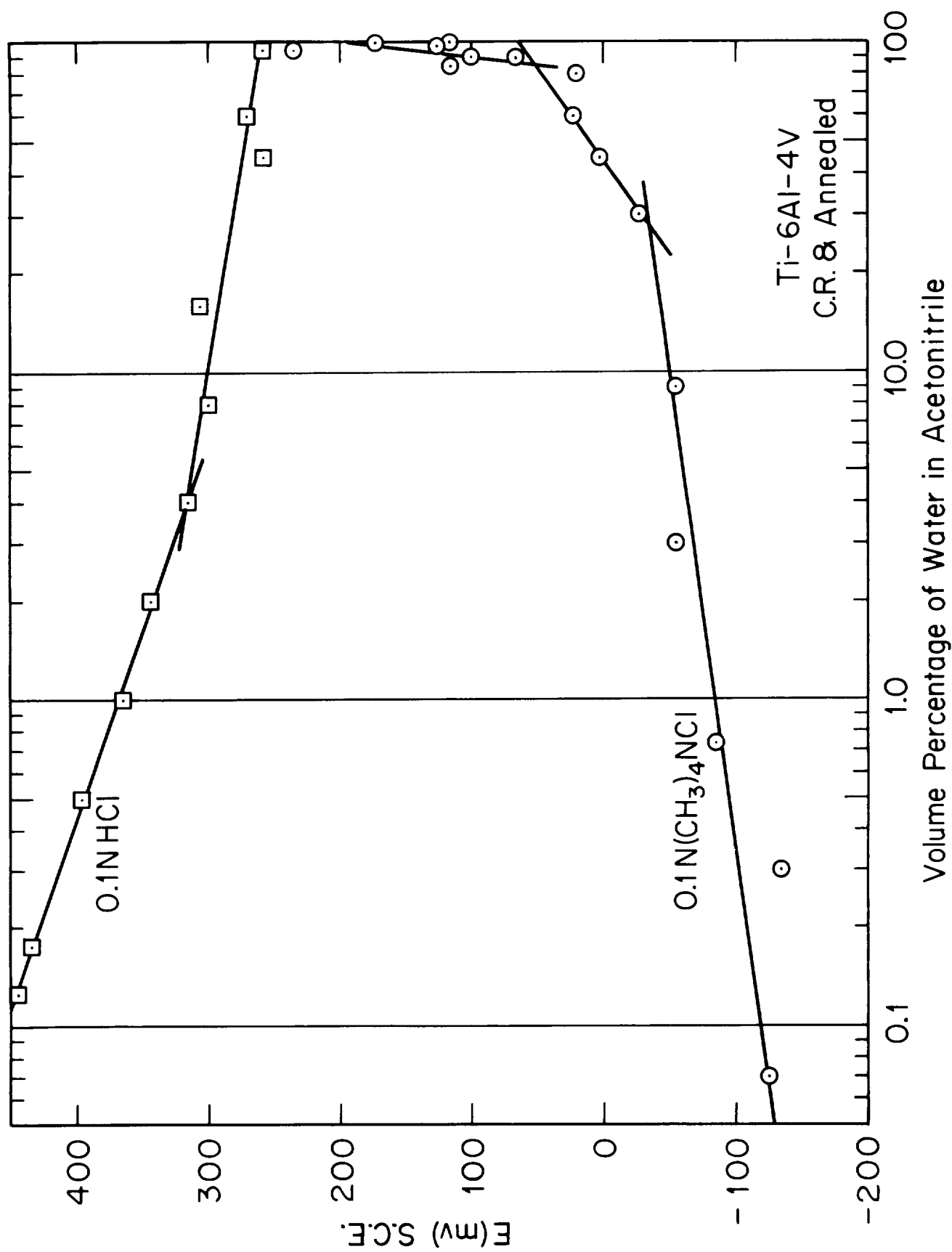Figure 8 Comparison of time to failure with one-hour electrode potential value.
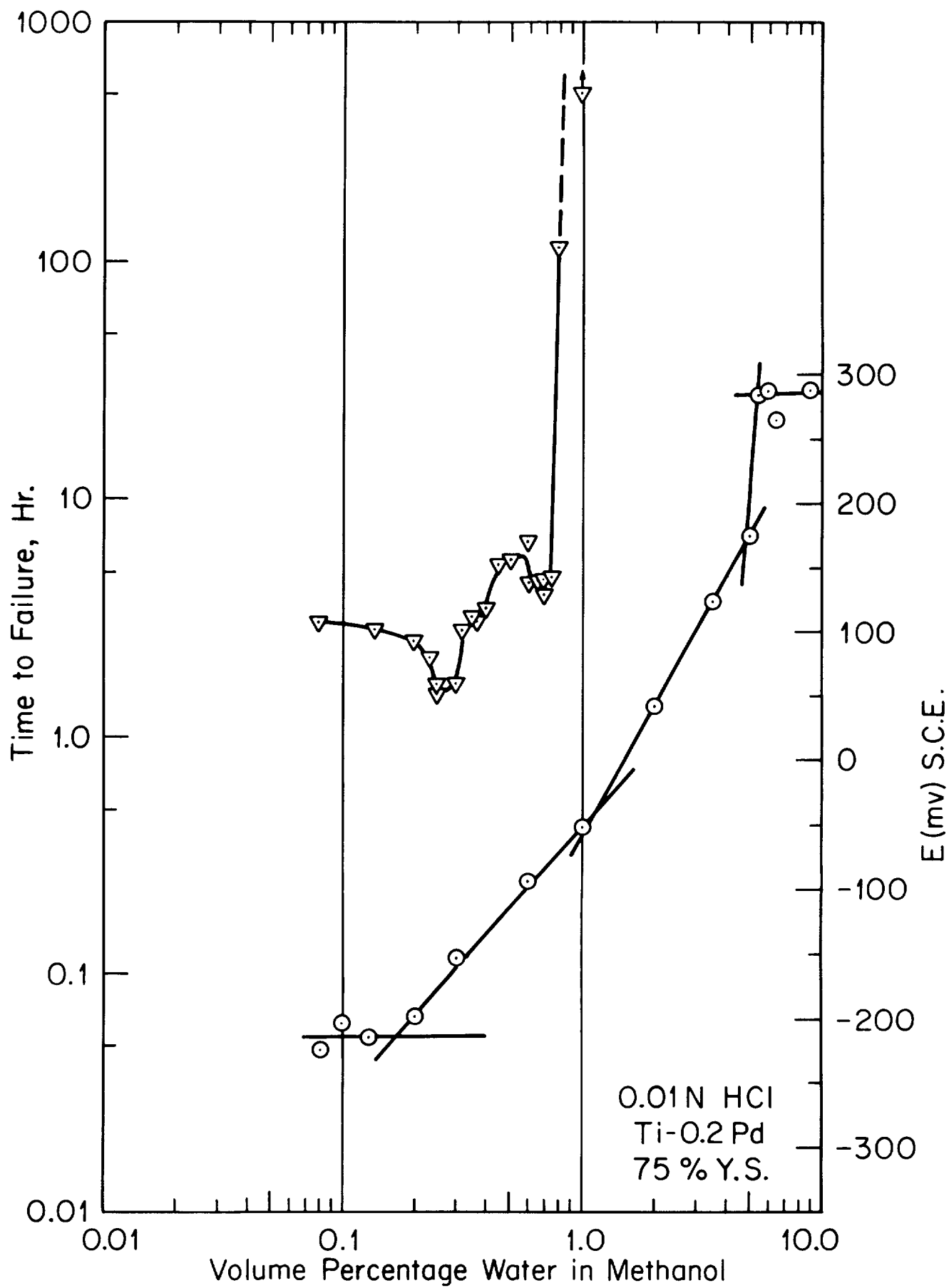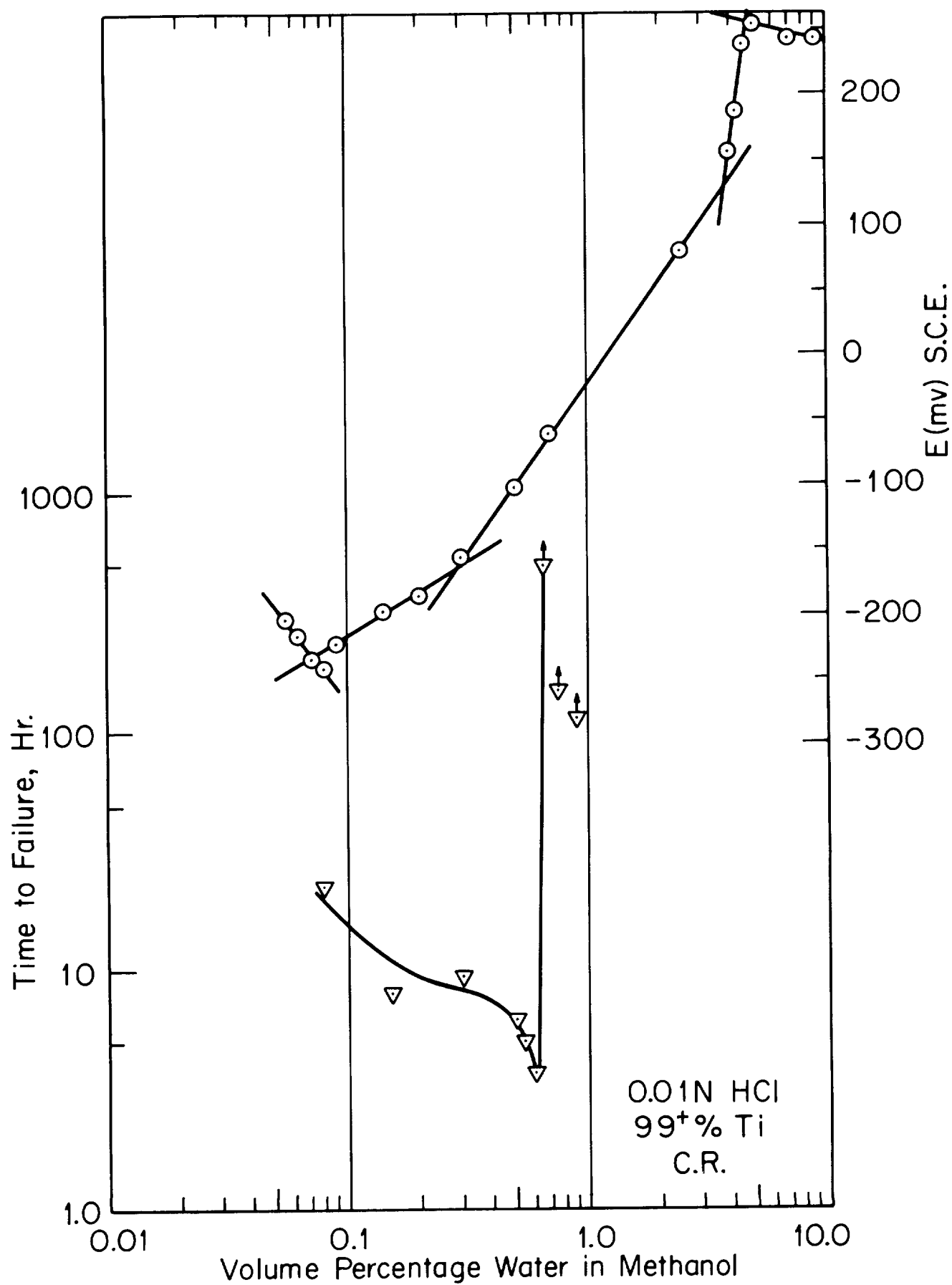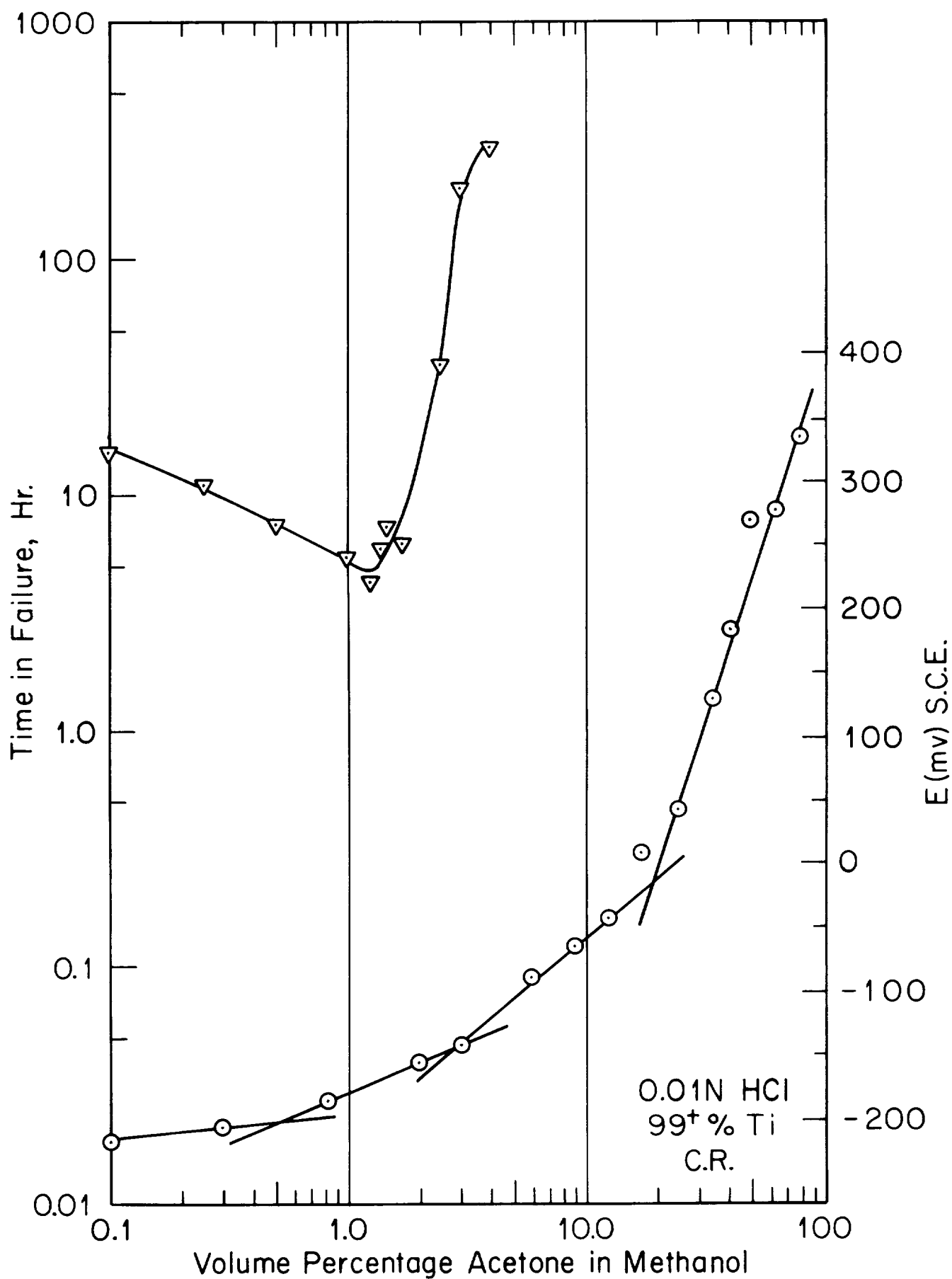
Figure 9 Comparison of time to failure with one-hour electrode potential value.
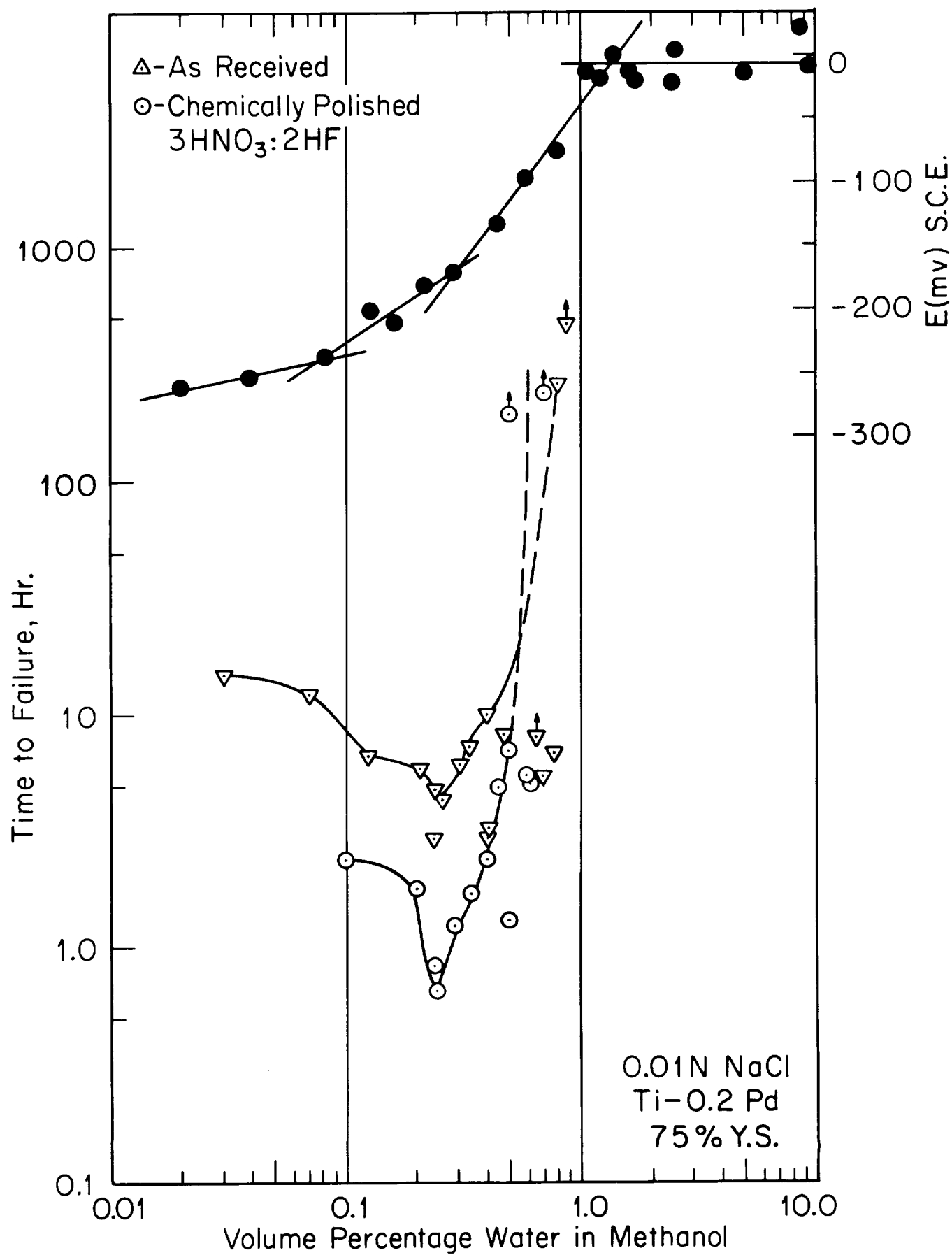
Figure 10   Comparison of time to failure with one-hour electrode potential value.
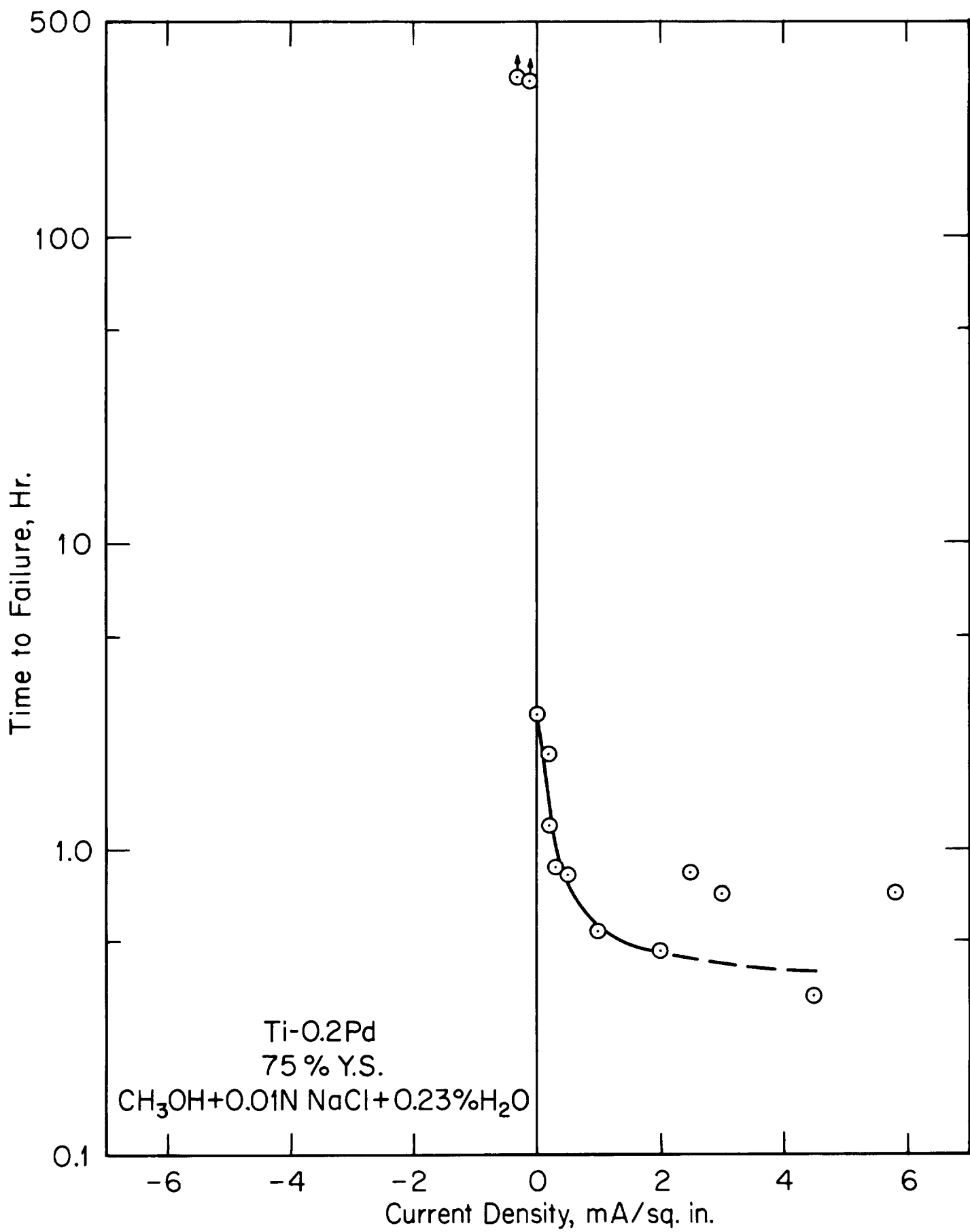
Figure 11 Effect of cathodic and anodic polarization on time to failure.
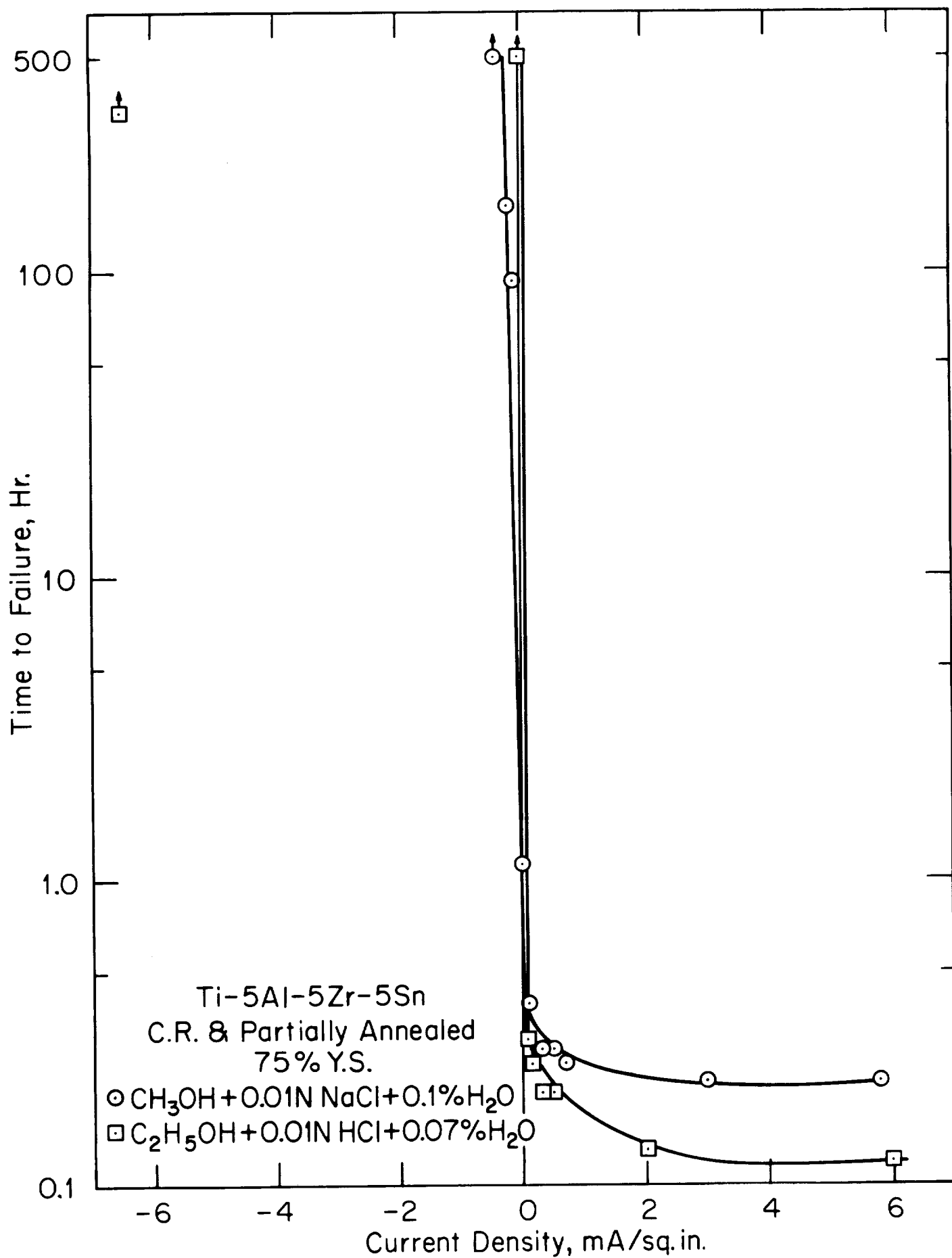
Figure 12   Effect of cathodic and anodic polarization on time to failure.
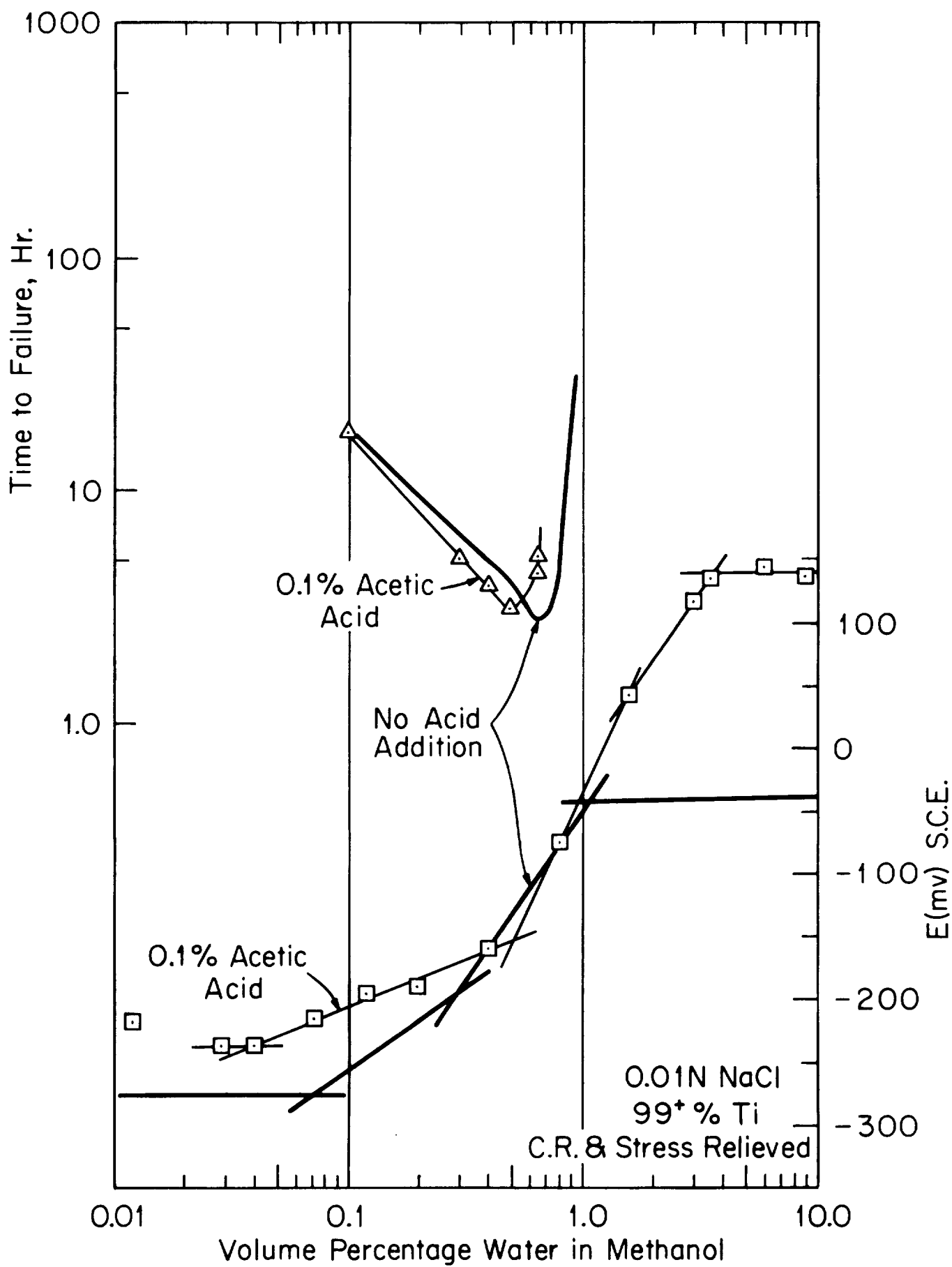
Figure 13 Comparison of time to failure with one-hour electrode potential value.
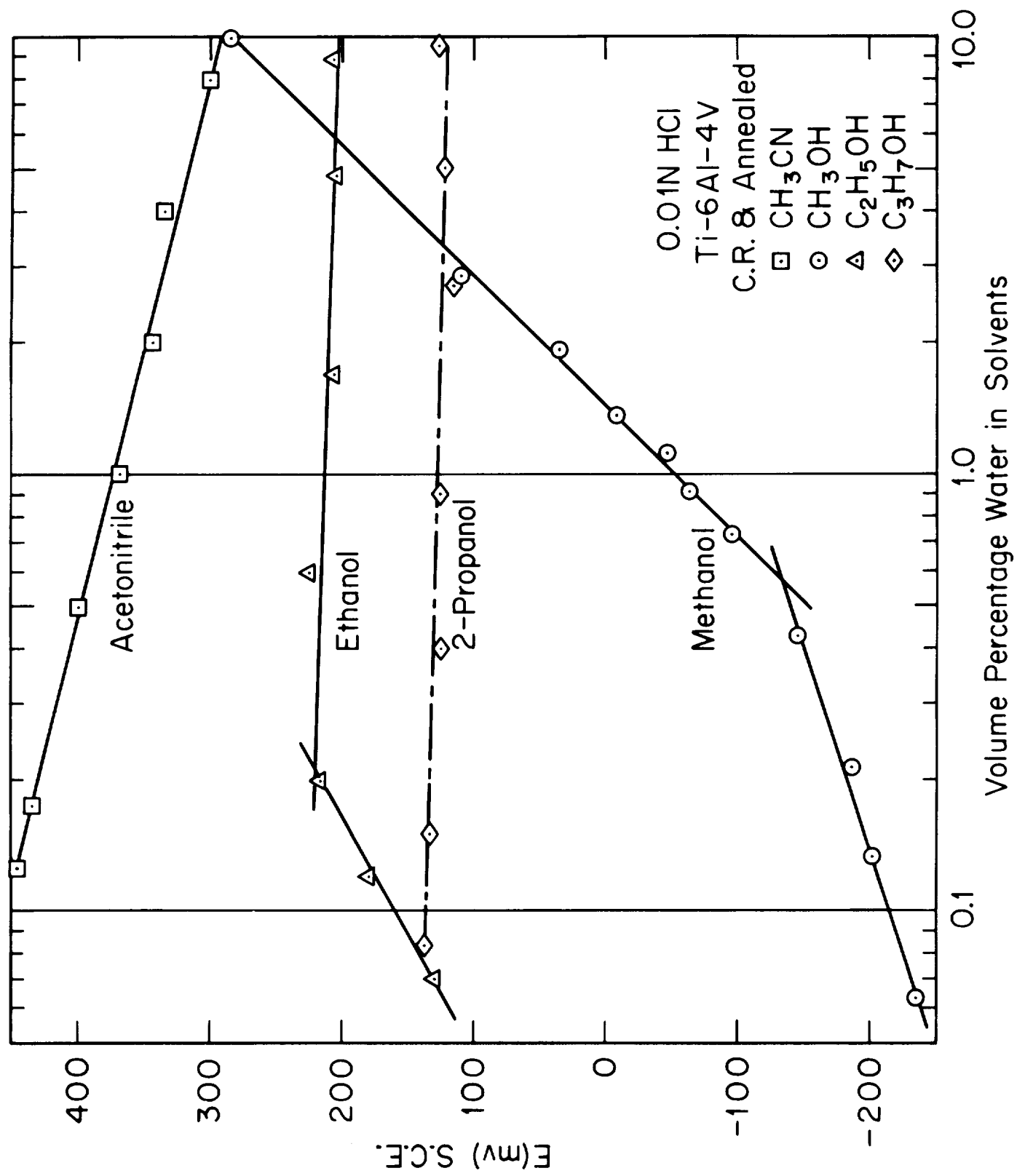
Figure 14 Comparison of one-hour electrode potential values for several solvents.

Figure 15 Comparison of time to failure with one-hour electrode potential values.

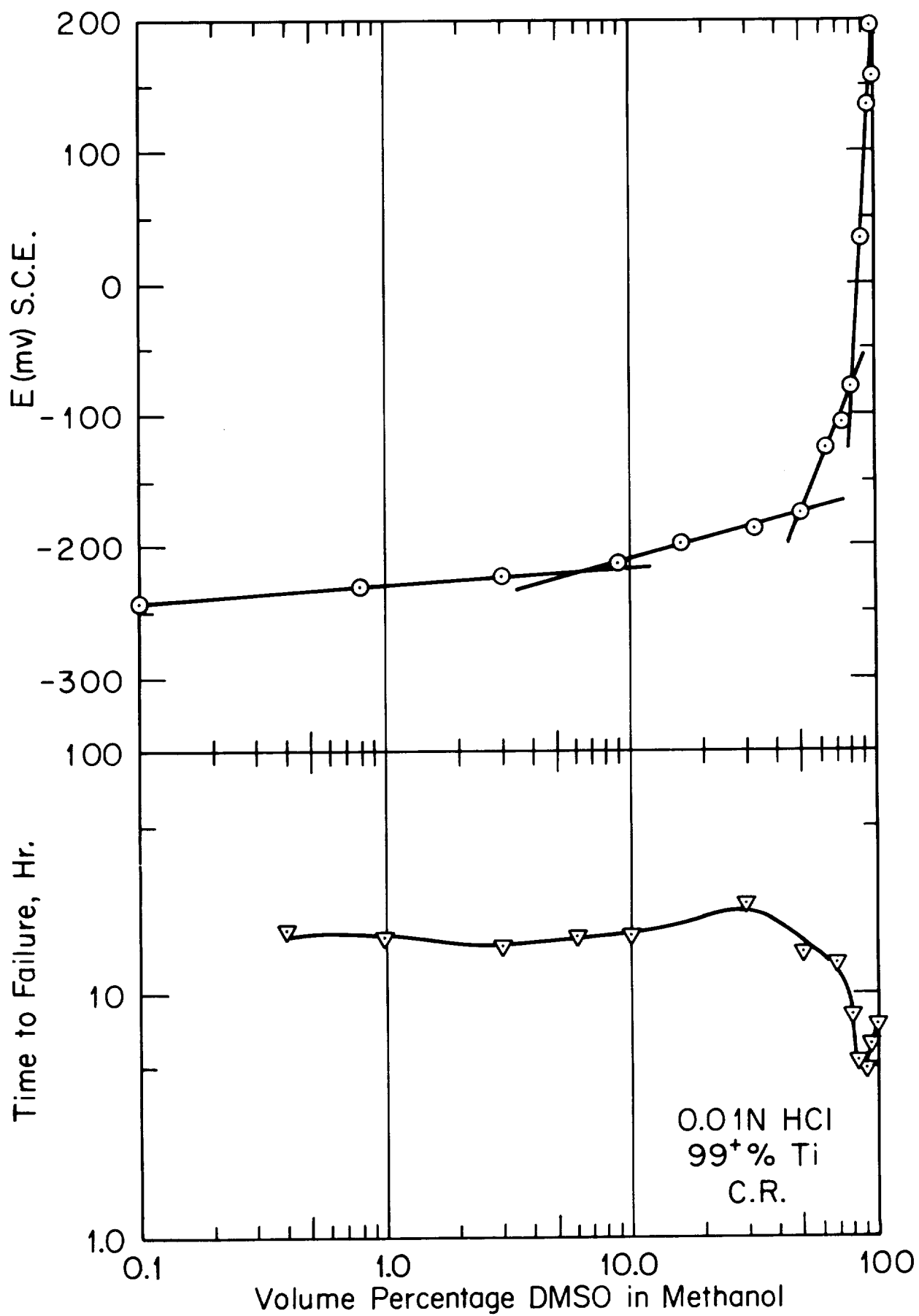Figure 16   Comparison of time to failure with one-hour electrode potential values.
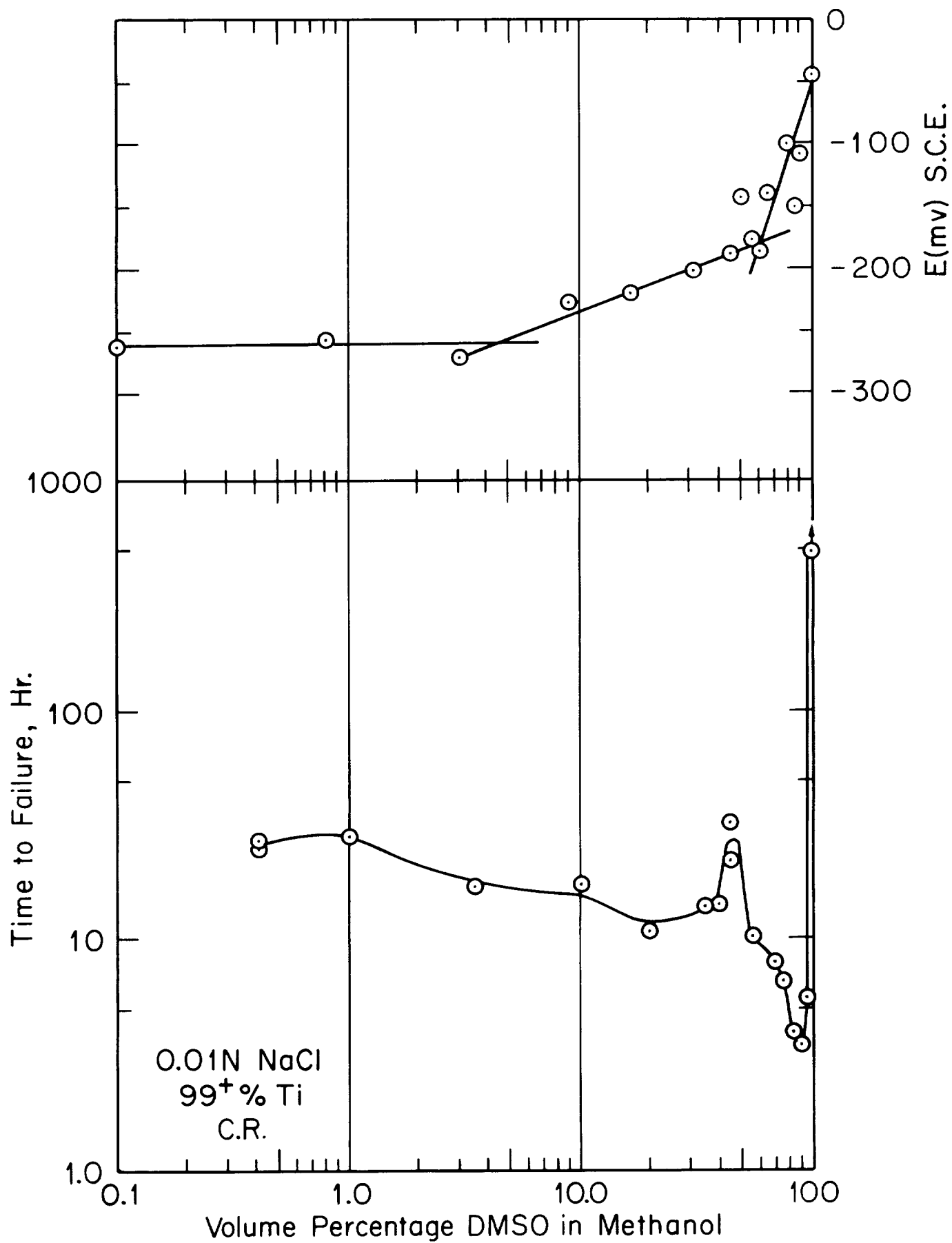
Figure 17   Comparison of time to failure with one-hour electrode potential values.

Figure 18 Effect of hydrochloric acid and tetramethylammonium chloride on electrode potentials.

Figure 19 Comparison of time to failure with one-hour electrode potential values.

Figure 20 Comparison of time to failure with one-hour electrode potential values.

Figure 21   Comparison of time to failure with one-hour electrode potential values.

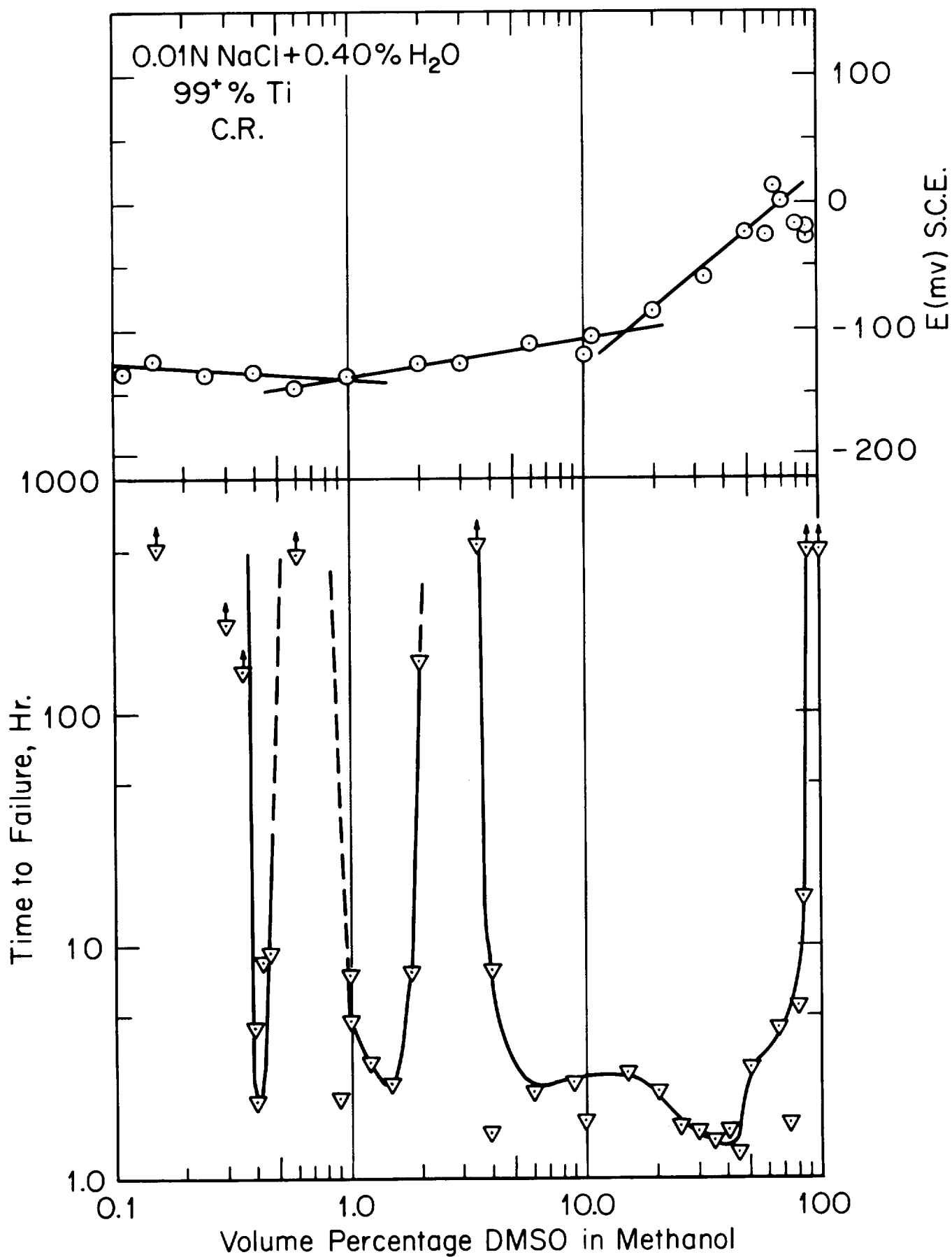Figure 22 Comparison of time to failure with one-hour electrode potential values.

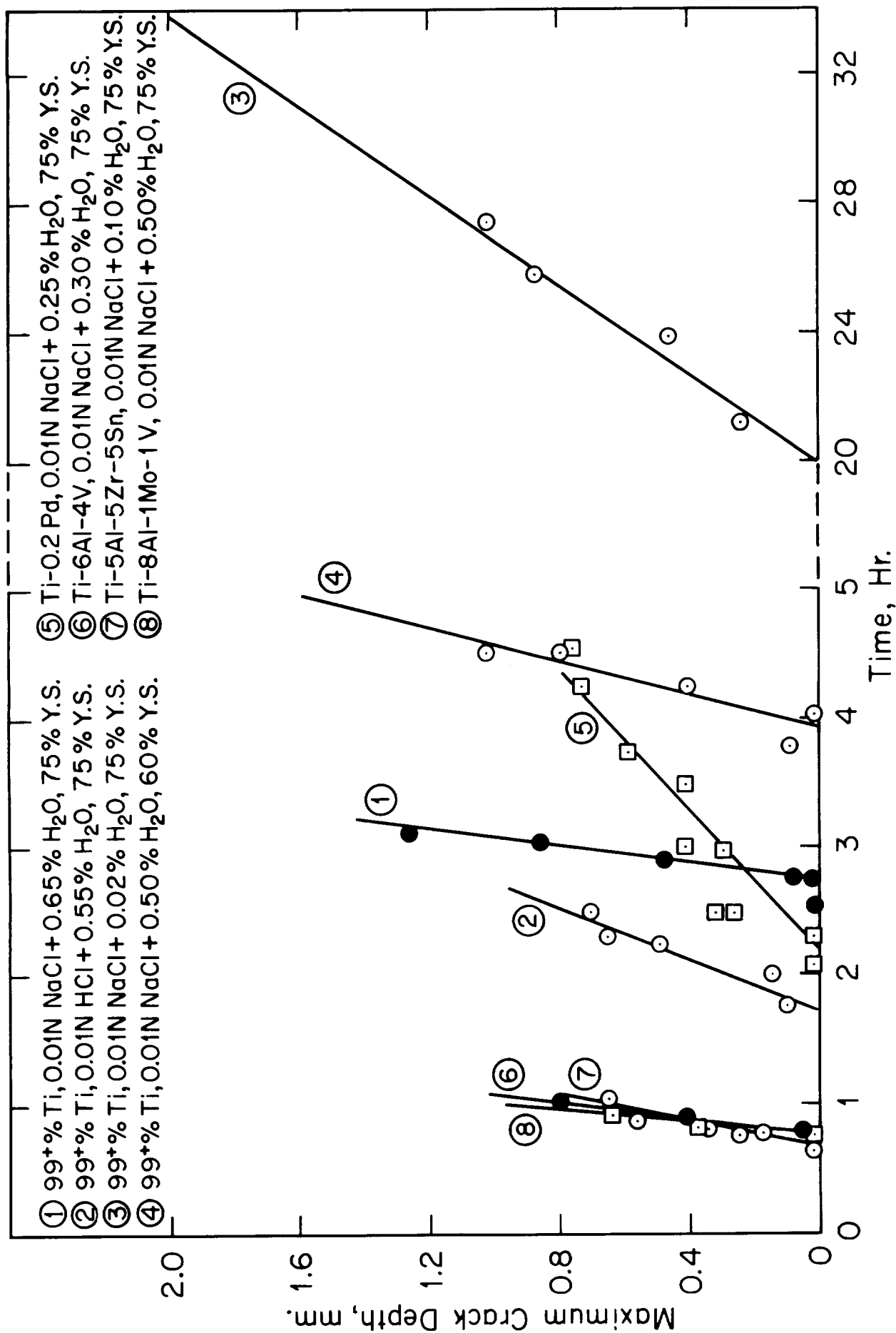Figure 23 Comparison of time to failure with one-hour electrode potential values.

Figure 24 Crack growth in foils for several alloys and solutions.